PROCEEDINGS

OF THE

NATIONAL ACADEMY OF SCIENCES, INDIA

1968

VOL. XXXVIII SECTION—A PART I & II

NATIONAL ACADEMY OF SCIENCES, INDIA
ALLAHABAD

PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
INDIA
1968

VOL. XXXVIII SECTION—A PART I & II

Role of soil microbiology in the maintenance and improvement of land fertility

By
B. N. SINGH
Central Drug Research Institute, Lucknow

The increase in crop production is of prime importance in India. Emphasis has been given, so far, to soil survey, application of fertilizers, plant breeding and the use of pesticides. Although the growth and health of crops are greatly affected by the activities of the micro-population in soil, detailed study of soil microbilogy has been neglected in tropical and semi-tropical regions of the world.

Soil microbiology includes the study of bacteria, fungi and actinomyces, algae, protozoa, viruses and numerous other micro-organisms that are present in soil. Although the microbes are perhaps the oldest inhabitants of this world, the entire history of soil microbiology covers no more than a period of ninety years. Soil microbiology arose in an attempt to account for certain chemical processes, such as oxidation of ammonia and fixation of nitrogen, already shown by chemists to take place in soil. Thus, unlike the developmental history of botany and zoology, soil microbiology has had a highly atypical develodment. Morphology, taxonomy and ecology of micro-organisms harbouring different types of soils have not been properly studied.

It is well known that a fertile field soil in temperate zone contains teeming millions of a complex population of microscopic life. This population is not only large but also very varied. They are of great importance to crops since some of them are the agents that prepare the soluble food materials available to crops. Different types of micro-organisms differ very much in this respect so that not only the quantity but also the quality of the microbial population must have an important influence on crop growth. It is, therefore, important to answer two basis questions : (1) What are the common species of micro-organisms present in different types of soils ? and (2) Why are they common ? Answers to these questions are necessary for a rational approach of encouraging the predominance of the more useful species and the suppression of the harmful types and so improve soil's fertility. Any attempt to produce the beneficial changes in the soil population, by encouragement of organisms producing desireable biochemical activity or by the suppression of the pathogens, must take into consideration the complex interaction between different groups of micro-organisms. The effect that micro-organisms

and their metabolic products have on one another are very varied and complex. The interactions may be due to straight forward competition between organisms with the same needs occupying the same habitat, or to the effect that the metabolic product of one may have on the existence of the other or to the fact that one group of organism prey upon the other. The dominance of certain groups and the prevalence of organisms having specific effects, whether beneficial or harmful, will determine what role they will play in a particular soil.

Micro-organisms in soil are not haphazard assembly, but form communities, the composition of which is determined and limited by environmental factors such as the quality and availability of food materials, pH, moisture, aeration, temperature etc. The soil environment is one of the most dynamic sites of biological interaction in nature. The abundance of micro-population reflects the fact that a fertile field soil is peculiarly favourable environment for micro-organisms. The interdependence of soil-micro-organisms and the physico-chemical conditions of the soil must be fully appreciated if any progress is to be made in understanding the problems relating to soil fertility.

It is well known that in tropical soils organic manure, added to soil in order to maintain the tilth and water holding capacity of the soil, repidly disappears because of oxidation due to micro-organisms, and thus leading to soil erosion. Study of micro-flora and micro-fauna may lead to the discovery of suitable types of fertilizers or in slowing down the microbiological processes and thus making the nutrients available to plants for a longer time. Microbiology of 'usar' lands may help in the establishment of micro-organisms that are needed for maintaining soil fertility. In delta regions, where large quantities of alluvial soils are transported, it is important in their reclamation to determine the factors that will lead to the establishment of useful micro-organisms needed to build up the fertility of these soils.

When a soil is waterlogged, as happens in rice fields, there is a decrease in the abundance of aerobic micro-organisms and a parallel stimulation of the anaerobes. This change is due to the disappearance of free oxygen as a result of its utilization by oxygen-requiring micro-organisms. There is a shift from aerobic to anaerobic transformations. A detailed study of the microbiology of waterlogged soils has yet to be undertaken. In this connection, it may be of interest to recall the theory of "partial sterilization" of Russell and Hutchinson (1909). According to this theory, "soil sickness" is due to an excessive numbers of active (trophic) protozoa which by their phagocytic action restrict bacterial processes going on in the soil and the remidial effect of "partial sterilization" by killing these protozoa by sterilizing agents. Although it has been shown by Singh and Crump (1953) that beneficial effect of "partial sterilization" is not due to the killing of amoebae, numerically the most important group of soil protozoa in temperate soils that feed selectively on bacteria, it would be of interest to study the role of protozoa in waterlogged soils. Due to water-logging ciliates and other protozoa, which do not lead an active life in field soil due to the lack of sufficient moisture, may become abundant and interfere with the transformations carried out by bacteria. It has been suggested that in paddy-fields the increase in nitrogen is due to algal growth. The algae, by photosynthetic process, also liberate molecular oxygen and thus provide part of the oxygen requirement of the submerged roots.

Next to water, oxygen and carbon dioxide, nitrogen is needed in largest quantity by crops. The demand for nitrogen is bound to increase owing to rising

world population. The resources of industrial power to produce artificial nitrogenous fertilizers are not inexhaustable in the long run. Leaching and denitrification are bound to aggravate the situation. Therefore, the possibility of supplying nitrogen to the soil by biological nitrogen fixation must be thoroughly explored. The work on root nodule bacteria has already produced results of practical importance to agriculture in some countries.

According to certain Russian microbiologists, it is possible to increase soil fertility of some Russian soils by the application of 'azotobacterin' and 'phosphobacterin'. The emphasis is placed that local strains of these bacteria are better than "All Union" strains issued by the Institute of Agricultural Microbiology in Leningrad. According to Russian microbiologists, the fertilizer trials conducted in the United States were unsuccessful because Russian strains of *Azotobacter* were used. The successful establishment of useful micro-organisms in field soil is by no means easy because of the existence of antagonistic micro-organisms. However, the work of Russian workers does suggest that the subject of bacterial fertilizers should not be neglected.

Russell and Hutchinson (1909) showed that increased fertility of partially sterilised soil by volatile antiseptics was due to a great increase in microbiological activity. They suggested that it was brought about due to changed equilibrium between the components of the micro-population. The moce recent work at Rothamsted Experimental Station, England on "partial sterilization" by means of steam and formalin, under field condition, has clearly shown that the qualitative and quantitative changes brought about by these treatments in the microbial population persisted for more than a year. Therefore, the dominance and persistence of micro-population brought about by external factor or factors will greatly effect soil fertility.

Study of polysaccharides and related compounds, produced by micro-organisms, has an important bearing on soil crumb structure and humus formation in soil. Microbiology of 'rhizosphere' and 'mycorrhiza' has an obvious practical importance on the growth of crops and the prevention of certain root diseases caused by biological agents. The effect of pesticides—herbicides, insecticides, fungicides—on non-pathogenic microflora and microfauna must be carefully determined otherwise some important group or groups of micro-organisms needed for nutrient transformations be eliminated and the crop yield reduced.

The available techniques of increased crop production are nearly exhausted and the future can hold promise through basic research. An integral and important part in any plan of increased crop production in India should be an elaborate scheme for long term intensive research in soil microbiology. A proper beginning can be made by creating a centre for soil microbiological research consisting of specialists in the different branches of microbiology and allied sciences. This will help in contributing to an integrated picture of soil science and soil conservation. The knowledge so gained may be utilized for practical agriculture. In addition, the microbiological research centre should train microbiologists interested in tropical and semi-tropical soil microbiology. Suitably trained personell are badly needed for co-ordinating schemes on all India basis and for creating centres of soil microbiology in the Provinces.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968

Effect of washing on basic slags

By

N. R. DHAR & B. S. GUPTA

Sheila Dhar Institute, University of Allahabad, Allahabad

Introduction

From the point of view of the availability of the elements, present in basic slag, to the plants, solubility and hydrolysis in water play important role. Scidenstucker[1], Walter[2], Sherman and Grant[3], Gericke[4] and others have concluded from their experiments with basic slags, that enormus quantities of water would be needed for the complete removal of phosphorus and other elements from high grade basic slags. But there is considerable difference of opinion as to the usefulness of low grade basic slags. The authors have studied this problem and have presented their observations showing that low grade basic slags are also useful as much as high grade basic slags.

Experimental

10 grams of hundred mesh sieved powder basic slag in 100 ml. conductivity water were taken into 250 ml. conical flask and was shaken for one hour in a mechanical shaker and then filtered atonce. Aliquot portions were taken for the estimation of P_2O_5 and basic constituents in the filtrate[5-9]. The residue remaining in the funnel was transferred to the flask again by means of a glass rod and the requisite amount of water was added. The extraction was repeated hundred times without any intervals between the extractions in a series and the cycle of operation was carried out with as much regularity as possible. The residue of basic slag was analysed by the help of [5-9]. The electrical conductivity was determined with the help of the instrument known as Kholaransch Slide Wire Cat. No. 4258, Leeds and Northrup, Philadelphia, U. S. A. The pH of all solutions were measured by the Beckman Glass Electrode, pH Meter, Model H-2, manufactured by Beckman Instrument Inc., California, U.S.A.

Discussion

The effect of washing and the behaviour of the different extracts regarding their pH, Specific Conductivity and the concentration of P_2O_5 has been represented in Fig. No. 1 to 3. From a close study of the graphs, it appears that the amounts of P_2O_5 decrease from the first extraction to the last. The electrical conductivity also likewise decreases with increasing the numbers of extraction. The pH of German and Belgium Basic Slags increase upto 10 extractions and then decrease slowly. The pH of Indian Basic Slags remain constant or slightly increase from original and this is due to more lime passing into solution. It has further been observed that the pH of the successive extracts of Kulti, Durgapur and Rourkela Basic Slags are lower than the pH of the first extract and the corresponding extracts of Tata Basic Slag. This is due to the fact that comparatively more lime has passed into the solution in the former extracts than in the subsequent extracts, while very slight change has occurred in the P_2O_5 concentrations, the amount of which is also very small. The pH of the extractions of basic slags is 7 after 95th and upward extracts. From this observation it appears that all

soluble basic materials present in basic slags washed off during the washing. This is further supported by the analysis of residual basic slags as shown in table No. 2. The pH of residue, has been observed after 100 extractions, is to increase alkalinity simply by keeping the residue in contact with water for 24 hours. This is probably due to the hydrolysis of complex basic silicates and phosphates present in the residue of basic slags.

TABLE 1

Analysis of different basic slags

Symbols	Tata basic slag	Kulti basic slag	Durgapur basic slag	Rourkela basic slag	German basic slag	Belgium basic slag
SiO_2 etc.	15·6846	16·9677	20·1640	22·4600	11·4665	11·9867
Iron (Total)	10·8265	9·8100	12·1884	11·5966	9·1263	10·0216
Fe_2O_3	3·8000	4·1000	5·2900	5·6466	4·1233	4·9888
FeO	10·4678	8·9000	10·8764	9·8000	7·9999	8·3688
Al_2O_3	5·4320	6·4860	6·8748	6·3646	3·0678	2·9646
CaO	38·6946	40·1800	37·7785	40·0000	42·3467	41·6846
MnO	2·9079	2·9978	4·6633	3·1674	4·8736	4·1844
MgO	4·8486	4·1346	5·6726	6·0174	4·9800	4·6788
K_2O	0·6474	0·3364	0·5644	Traces	Traces	Traces
Halides	0·1768	0·1967	0·2233	0·1884	0·1067	0·0988
Sulphur	0·3674	0·4678	0·6078	0·6446	0·2222	0·2567
V_2O_5	0·4881	0·4136	0·3468	0·3394	0·6438	0·5488
Cr_2O_2	0·3973	0·3688	0·2988	0·2767	0·4678	0·3999
TiO_2	0·3126	0·2566	0·2333	0·2188	0·4784	0·2999
CuO	0·0053	0·0044	0·0044	0·0038	0·0048	0·0088
ZnO	0·0064	0·0056	0·0086	0·0047	0·0056	0·0060
MoO_3	0·0080	0·0088	0·0100	0·0093	0·0108	0·0102
P_2O_5 (Total)	7·7380	4·1680	3·4868	2·0684	17·8683	16·6640
P_2O_5 (Available)	4·1020	2·0340	3·4868	2·0684	7·9672	7·6360
Sp. conductivity in mhos $X10^{-4}$	3·14	4·18	3·76	3·98	6·82	6·72
pH	9·50	9·70	9·15	9·65	8·85	8·75

TABLE 2

Analysis of different basic slags after hundred washings

Symbols	Tata basic slag	Kulti basic slag	Durgapur basic slag	Rourkela basic slag	German basic slag	Belgium basic slag
SiO_2 etc.	13·2468	14·0650	16·2460	17·1344	9·99688	10·2068
Total Iron	9·9678	8·8346	11·2000	10·6000	8·42666	9·2067
Al_2O_3	4·8677	5·7688	5·8123	5·6044	2·7468	2·7000
CaO	32·7687	33·0366	33·0288	33·0000	32·6844	31·6000
MnO	2·1234	2·2000	3·1678	2·2888	3·3660	3·2000
MgO	3·1333	2·9688	3·3784	3·6444	2·8864	2·7947
V_2O_5	0·3546	0·3279	0·2867	0·2846	0·5677	0·4800
Cr_2O_3	0·2116	0·2456	0·1677	0·1700	0·1078	0·1238
TiO_2	0·2887	0·2284	0·2186	0·2000	0·3146	0·2898
K_2O	Traces	Traces	Traces	—	—	—
CuO	,,	,,	,,	Traces	Traces	Traces
ZnO	,,	,,	,,	,,	,,	,,
Halides	,,	,,	,,	,,	,,	,,
Sulphur	,,	,,	,,	,,	,,	,,
P_2O_5(Total)	6·8868	3·6596	2·9974	1·7374	16·0820	15·0000
pH of the residue after one hour	7·00	7·00	7·00	7·00	7·00	7·00
pH of the residue after 24 hours	7·25	7·30	7·20	7·25	7·10	7·05
Loss of P_2O_5 in percentage	11·03	12·22	14·03	16·00	10·00	10·00

It is evident from the graph No. 3 that the P_2O_5 concentration changes slightly in the different extracts to the 10th extract but later on it falls rapidly and only in traces are found between the 45th to 70th extracts. As the grams of P_2O_5 per litre of water in the first extract are 0·0144, 0·0137, 0·00768, 0·0048, 0·0042 and 0·0035 of German, Belgium, Tata, Kulti, Durgapur and Rourkela Basic Slags respectively. The P_2O_5 concentration has been found in traces in the extract of 70, 70, 55, 55, 45 and 50 of the German, Belgium, Tata, Kulti, Durgapur and Rourkela Basic Slags respectively.

Fig. No 1.

pH and Sp. Conductivity of Filterate

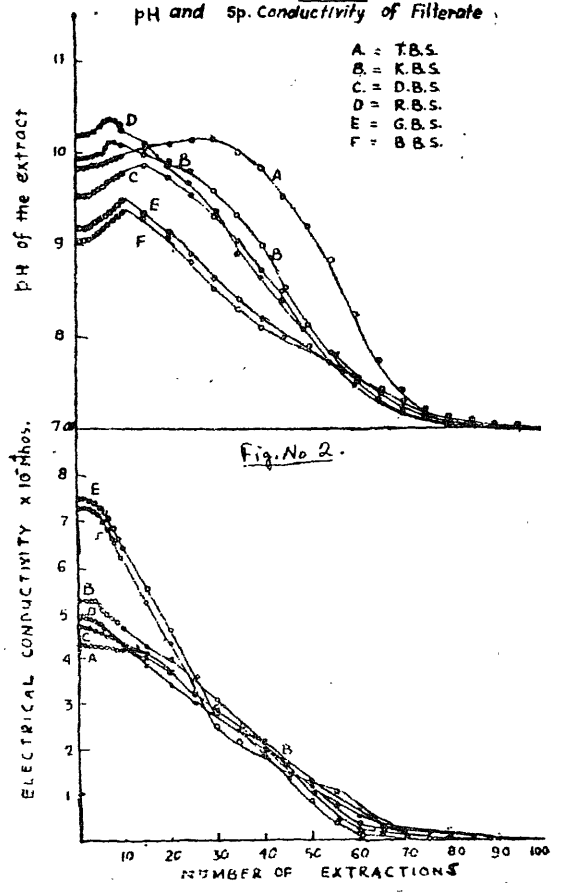
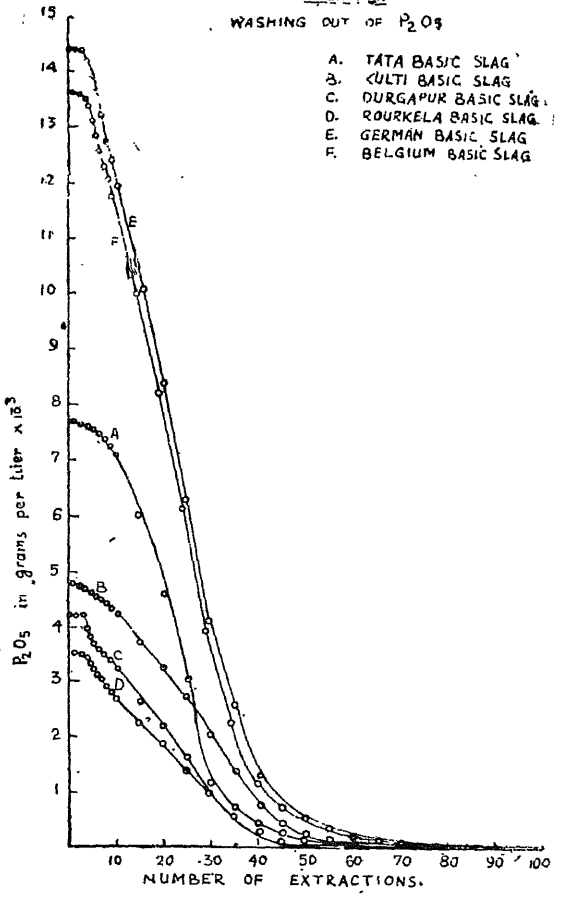


Fig. No 2.

Fig. No 3.

WASHING OUT OF P_2O_5



From table No. 2, it is clearly observed that all trace elements are soluble in water and may be utilized for crop production. After twenty-four hours, water further able to decompose the insoluble materials into soluble ones. So taking into account the lack of absorptive power and high degree of leaching in majority of tropical soils, it is highly useful to apply to them these basic slags. It has been observed by several workers[10-13] that from soils treated with superphosphate considerable amounts of phosphates are washed away when rain fall is large. Recently Papadakis[14] reported that the leachsequence is based on the composition of the clay fraction and the presence of certain soluble substances.

From the foregoing considerations and the behaviour of basic slags in water, it can be concluded that all basic slags, low or high grade basic slag, are ideally suited and may be applied at practically any time during the non growing period, thus permitting selection of a convenient time, in autumn, winter, or early spring and all the elements present in basic slag, are not leached from the soil by rain or drainage. Hence our investigations with European and Indian basic slags establish that Indian low grade basic slags may also be useful for agriculture.

Summary

The effect of washing the different basic slags has been studied and it has been observed that not only calcium and phosphorus are washed off but Potassium, Copper, Zinc, Magnesium, Manganese, Titanium, Chromium, Vanadium, Molybdenum etc. pass into the filtrate, low grade basic slags may also be useful in agriculture.

References

1. Scidenstucker. *Kunstdunger u. Lein*, **28** : 293-6, 1931.
2. Walter. *Kunstdunger u. Lein*, **28** : 338-41, 1931.
3. Sherman, C. W. and Grant, N. J. *J. Metals*, 1, No. 11 *Trans.* 898-903, 1949.
4. Gericke, S. *Bilanz der Mikroelemente. Centre int. Engr. Chem. Ve Assembl. gen. Rapp.*, **1** : 185-193, 1956.
5. Scott, Wilcred, W. *Compare.* Standard Methods of Chemical Analysis. 5th Ed., 1946.
6. Snell and Snell. *Compare.* Colorimetric Methods of Analysis. *D. Van Norstrand and Co.*, 1958.
7. Vogel, A. I. *Compare.* Quantitative Inorganic Analysis. 2nd Ed., 1959.
8. Washington, H. S. *Compare.* The Chemical Analysis of Rocks. 4th Ed., 1930.
9. Dyer, B. *Trans. Chem. Soc.*, **65** : 115-167, 1894.
10. Schmitt, L. *Das Superphosphate*, **9** : 103-108, 1933.
11. Iverson, K. *Tidsskr. Planteavl.*, **50** : 106, 1945.
12. Hall, A. D. *Book of Rothamsted Expts.*, 238, 1905.
13. Ayres, A. S. and Hagihara, H. H. *Hawaii Plant Rec.*, **56** : 255-75, 1963.
14. Papadakis, J. *Int. Soil Conf. N. Z.*, 45-49, 1962.

Proc., Nat. Acad. Sci., India, 38(A), I & II, 1968

Role of fertilization in soil fertility as measured by carbon-di-oxide evolution and bacterial population

By

HARPAL SINGH *and* S. C. SEN*

Planned fertility studies are useful in formulating manurial recommendations for obtaining higher crop yields. Soil fertility is directly correlated with the rate of carbon-di-oxide evolution and bacterial population. The present investigations were planned with a view to obtaining information for preparing a manurial schedule for the sugarcane crop in the loam soils of Kanpur.

Biological activity of the soil is one of the measures for fertility. The rate of evolution of CO_2 is due to the activity of heterotrophic and autotrophic bacteria utilizing soil organic matter as a source of energy and also due respiration of plant roots which is an index of the fertility of the soil.

Wahhab and Bokhari (1955) established correlations between wheat yields and evolution of carbon-di-oxide, Doyanenko (1950) found increased crop yields by increasing the carbon-di-oxide content of the layer of air near the soil. Brieje (1959) obtained better yields by increasing the percentage of CO_2 in the air between growing plants. Russel and Appleyard (1915) observed that the rise in bacterial number was accompanied by rise in the CO_2 evolution and some-what later by the rise in the nitrate content. Acharya and Jha (1954) reported higher carbon-di-oxide production in soils receiving organic matter and phosphates. Dhar (1936) also reported similar results.

The soil subsists on the products of microbial activity, for the micro-organisms are continually oxidising the dead plant remains and leaving behind the nutrients in a form available to the plants. Sinha, Ghosh and Singh (1958) observed significant correlations between nitrogen metabolism and microflora population.

Material and Methods

The surface soil of top nine inches was collected from different places from the field where trials was to be laid out, mixed well, to make a composite sample, ground and passed through 0·2 mm seive ; 25 lbs. soil was taken and the calculated quantities of fertilizers and manures based on the different treatments were applied. The pots were arranged at random in three replications and moisture level was mantained at 15 per cent during the course of investigation. Carbon-di-oxide was determined by Petten Kofer's method. Total bacterial population was developed on Thorton's agar media by incubating the peteridishes at 20° to 40°C. Carbon-di-oxide evolution studies were carried out in two different seasons when the temperature was low during winters and high during summers.

Present Address : 1. Dr. Harpal Singh, Jassa Ram, Hardwar, Saharanpur.
2. Dr. S. C. Sen-113/226 Swarupnagar, Kanpur.

Treatments

A. 120 lbs. nitrogen per acre as ammonium sulphate.

B. 120 lb. nitrogen per acre as ammonium chloride.

C. 120 lb. nitrogen per acre as ammonium sulphate+80 lb. P_2O_5 as superphosphate.

D. 120 lb. nitrogen per acre as ammonium chloride+80 lb. P_2O_5 as superphosphate.

E. 120 lb. nitrogen per acre (80 lb. as ammonium sulphate+40 lb. as molasses and press mud).

F. 120 lb nitrogen per acre (80 lb. as ammonium chloride+40 lb. molasses and press mud).

G. 120 lb. nitrogen per acre (80 lb. ammonium sulphate+40 lb. as molasses and press mud)+80 lb. P_2O_5 as superphosphate.

H. 120 lb. nitrogen per acre (80 lb. as ammonium chloride+40 lb. as molasses and press mud)+80 lb. P_2O_5 per acre as superphosphate.

I. Control.

Experimental Findings and Discussion

A perusal of data in Table I and II show that maximum quantity of CO_2 was evolved during the first five days of incubation irrespective of treatments. Comparatively higher amounts of CO_2 was evolved in treatments where organic manures like press mud and molasses were added along with sulphate of ammonia in presence of phosphatic fertilizers. This may probably be due to increased supply of energy and consequently improved metabolism of haterotrophic bacteria. In the beginning, the rate of CO_2 evolution was slightly slow in the soils treated with muriate ammonia presumbly due to the toxic effects of chloride ions. Later, this does not seem to have the adverse effect since after a lapse of fortnight upto a period of 30 days the CO_2 evolution was higher to that of ammonium sulphate treatment. The unmanured soil evolved least amount of CO_2 compared to the soils treated with netrogenous and phosphatic fertilizers alone or in combination with organic manure. The yield figures were directly correlated with the rate of CO_2 evolutiun and significantly superior in treated plots.

The application of phosphates with organic matter led to increased CO_2 evolution. It may be due to the acidic reactions created by the formation of organic acids during the decomposition of organic matter and making the phosphates more soluble and readily available for bacterial use. The increased rate of CO_2 evolution under nitrogen and phosphate treatment may be due to the increased quantities of body building materials of bacteria and corresponding increase in total bacterial population. The slower rates of CO_2 evolution in the biginning may be due to the bad effects of acids radicals which are toxic and more so with chloride radicals.

The rate of decomposition of manures indicates that during a period of 30 days organic matter is easily decomposed and hence molasses may be added about one month before planting, and during winter time between the addition of manures and planting of sugarcane, may be still more since at lowar temperatures decomposition rate is slow (Table I, CO_2 evolution at 20°C).

TABLE I

Mgms of CO_2 released under different treatments at 20°C.

Treatments	Mgms. of CO_2 after each interval in days 5	10	15	20	25	30	Total CO_2 in mgms
1	53·4	36·9	27·8	29·0	26·7	24·0	197·8
2	51·6	34·1	27·2	31·5	27·3	23·1	194·8
3	61·13	37·8	26·3	29·1	27·6	22·9	205·0
4	58·7	36·8	27·0	29·6	28·3	24·0	202·4
5	341·2	103·2	71·6	36·7	41·2	38·7	632·6
6	304·2	106·2	69·3	39·6	42·0	36·9	598·2
7	387·6	117·2	64·0	46·0	44·0	35·6	684·4
8	380·4	112·7	67·9	43·8	45·0	34·3	684·4
9	47·6	34·1	26·3	28·7	27·9	23·1	187·7

TABLE II

Mgms. of CO_2 released under different treatments at 40°C

Treatments	Mgms. of CO_2 after each interval in days 5	10	15	20	25	30	Total CO_2 in Mgms.	Yield/ acre
A	89·7	47·5	33·8	31·2	29·7	26·6	258·5	660·4
B	77·4	38·3	42·9	31·8	24·0	22·1	236·5	643·2
C	94·9	37·7	33·8	27·3	25·3	16·0	235·5	679·2
D	79·72	36·4	44·2	39·0	24·7	22·1	245·6	655·6
E	412·1	113·7	61·7	42·9	27·9	35·1	693·4	644·8
F	480·4	100·1	83·2	57·2	41·6	35·1	797·6	644·0
G	500·5	129·1	65·6	44·2	35·7	29·2	799·3	669·6
H	483·6	102·7	84·5	61·7	41·6	42·2	816·1	677·6
I	97·5	39·0	27·4	24·6	19·5	20·4	228·4	457·2

r=p. 6577.

Two varial series are positively correlated.

The harmful effects of acid radicals were noticed on the bacterial population under low and high ranges of temperatures in the beginning, *i.e.*, 24 hours after incumbation in all treatments except unmanured soil. The bacterial population increased from 5th day of incubation in case of treatments where organic matter was added with or without phosphates. This increase may be accounted for the reasons of readily available bacterial food *i.e.*, sugars and phosphates and consequent multiplication of asymbiotic bacteria and thereby increase in bacterial population. (Table III and IV).

TABLE III

Total bacterial population in millions per gm. of Soil at 20°C

Treat-ments	At start 1st day	After 24 hours	5 days	15 days	30 days	45 days
A	4·5	4·2	4·5	5·0	5·5	5·5
B	4·5	4·0	4·5	4·8	5·5	6·0
C	4·5	4·0	5·0	6·6	6·5	6·5
D	4·7	4·0	5·0	5·5	6·5	6·5
E	5·0	4·5	+15·5	15·0	12·5	10·5
F	5·1	4·5	+13·5	12·5	11·2	11·0
G	5·1	5·0	+17·5	15·0	13·5	11·5
H	5·0	4·5	+18·0	15·5	13·0	12·0
I	4·0	4·5	5·0	5·0	5·0	5·0

TABLE IV

Bacterial population in millions per gm. of Soil at 40°C

Treat-ments	At start 1st day	After 24 hours	5 days	15 days	30 days	45 days
A	4·5	4·0	5·0	6·5	6·0	6·0
B	4·5	4·0	5·0	6·5	6·5	6·0
C	4·5	4·5	5·0	7·0	6·5	6·5
D	4·5	4·5	5·5	7·5	7·0	6·5
E	5·5	4·5	27·0	23·0	14·5	10·5
F	5·0	4·5	26·0	24·0	15·0	12·0
G	5·0	5·0	28·5	25·0	18·0	13·0
H	5·0	5·0	27·0	24·5	16·5	12·5
I	4·0	4·5	5·5	5·5	5·0	6·0

Summary

Fertility studies were undertaken in loam soils of Kanpur by determining carbon-di-oxide evolution and total bacterial count under various nitrogenous, nitrogenous and phosphatic and nitrogenous+phosphatic+organic manures combinations. It has been observed that higher carbon-di-oxide production of soils could not be attributed to the influence of phosphates alone but also the organic manures (molasses and press mud). Higher sugarcane yields were directly proportional to the higher cabon-di-oxide production and total bacterial population. Acid radicals exhibit some toxic effects in the biginning which is more promounced with chloride ions. Molasses and press mud when applied to soil takes about 30 days for decomposition at higher temperatures.

Acknowledgment

The authors are grateful to S. N. Gundu Rao, the then Director of National Sugar Institutes, Kanpur for the facilities provided during the course of investigation.

References

Wahhab, A. and Bokhari, A. S. *Pakistan J. Sci. Res.* **7** : 129-133, 1955.
Doyarendo, A. G. *Pochvovedenie* **1** : 12–15 (R), 1955.
Brieje, C. J. *Meded Dir. Tuinh,* **22**: 670-674, 1959.
Russel, E. J. and Appleyard, A. *Jour. Agri. Sci.* 711, 1915.
Acharya, C. N. and Jha. *Jour. Ind. Soc. Soil Sci.* 2, 1, 1954.
Sinha, S. et al. *Bihar Acad. Sci.* 1958.
Dhar, N. R. *Proc. Ann. Conv. Sugar Tech.*, 15-19, 1936.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968

Nitrogen Loss During Nitrification of Urea in Different Types of Soils

By

S. K. GHOSH* *and* N. G. PAL

State Agricultural Research Institute, Calcutta-40

It has been stated by Allison[1] that losses of nitrogen occur quite widely in soils when they are under conditions of good aeration. The researches of Lipman and Blair[2], Russell and Richards[3] have shown that nitrogen in gaseous state is lost from soils when the conditions are favourable for oxidation. Field trials with different manures at Rothamsted[4] and elsewhere reveal that apporximately 70% of the added nitrogenous manures may be lost without benefit to the soil or the crop. Dhar and Ghosh[5] working with Indian Soils have also reported considerable loss of nitrogen from ammonium sulphate and urea when they undergo nitrification in soil under aerobic condition.

Further experiments on this type of nitrogen loss have been carried on by us with urea, when it undergoes nitrification in different types of soils collected from different parts of West Bengal.

Experimental

Surface soils 0″ to 6″ collected from three different soil types (*a*), (*b*) and (*c*) of West Bengal were well dried, powered and screened through a 100 mesh sieve. 150 grams, each of these three soil samples were accurately weighed in duplicate and taken in 500 ml glass beakers. Amounts of urea (A. R. quality) containing 1·50 grams and 0·75 grams of nitrogen were mixed with these soil samples in separate beakers. The contents of the beakers were thoroughly mixed and samples were taken out and analysed for their initial, total, ammoniacal and nitrate nitrogen contents. The mixtures were kept at the room temperature, stirred carefully by means of glass rod on alternate days and their moisture contents were maintained at nearly 30% level by adding distill water. Samples were taken at intervals of 20 days, 40 days, and 60 days for analysis of their total, ammoniacal and nitrate nitrogen contents respectively.

Total nitrogen was estimated by salicylic acid reduction method of Treadwall and Hall[6]. Ammoniacal nitrogen was determined by distilling soil with magnesia and nitrate nitrogen by reduction with Devarda's alloy. Mechanical and chemical analysis of soil samples were made before the start of the experiment by following the method of Piper[7]. Following results have been obtained :

**Present address* : Chief Soil Chemist, Fertiliser Corporation of India, Durgapur

TABLE I

Percentage composition of the oven-dried soil sample

	Ganga low land clay soil (Chinsurah, Dist. Hooghly)	Lateritic sandy clay loam soil (Suri, Dist. Birbhum)	Ganga reverine loam and clay loam soil. (Berhampore, Dist. Murshidabad)
	(*a*)	(*b*)	(*c*)
Coarse sand	0·30	30·14	–
Fine sand	8·52	32·01	–
Silt	35·06	20·02	22·14
Clay	56·00	18·06	21·48
Base Ex. Capacity	36·00 m.e.	13·12 m.e.	19·96 m.e.
Ex. Ca	19·88 m.e.	4·38 m.e.	13·24 m.e.
CaO	0·89	0·27	0·83
P_2O_5	0·08	0·05	0·24
K_2O	0·92	0·31	0·78
Total-N	0·069	0·055	0·071
NH_3-N	0·0012	0·0014	0·0028
NO_3-N	0·0064	0·0030	0·0088
pH	6·8	5·7	7·0

TABLE II

(*a*) *Ganga low land clay soil (Chinsurah, Dist. Hooghly)*

Treatments	Original amounts present in grams per 100 grams of the mixture	Final amounts obtained in grams per 100 grams of the mixture After 20 days	After 40 days	After 60 days
1. 150 gm. soil	Total-N=1·0463	1·0090	0·7350	0·3710
+1·50 gm. N	NH_3-N=0·0012	0·1523	0·3090	0·2480
as Urea	NO_3-N=0·0063	0·0150	0·0420	0·1260
2. 150 gm. soil	Total-N=0·5631	0·5530	0·4810	0·4540
+0·75 gm. N	NH_3-N=0·0012	0·0650	0·2010	0·0970
as Urea	NO_3-N=0·0063	0·0087	0·0560	0·1900

TABLE III

(*b*) *Lateritic sandy clay loam soil (Suri, Dist Birbhum)*

1. 150 gm. soil	Total-N=1·0325	0·1920	0·1590	0·1410
+1·50 gm. N	NH_3-N=0·0014	0·1145	0·0920	0·0730
as Urea	NO_3-N=0·0029	0·0106	0·0350	0·0760
2. 150 gm. soil	Total-N=0·5491	0·1910	0·1570	0·1510
+0·75 gm. N	NH_3-N=0·0014	0·1170	0·1060	0·0810
as Urea	NO_3-N=0·0030	0·0130	0·0210	0·0730

TABLE IV

(*c*) *Ganga Riverine loam and clay loam soil (Berhampore, Dist. Murshidabad)*

1. 150 gm. soil	Total-N=1·0469	0·1670	0·1450	0·1190
+1·50 gm. N	NH_3-N=0·0027	0·0627	0·0580	0·0420
as Urea	NO_3-N=0·0037	0·0123	0·0640	0·0640
2. 150 gm. soil	Total-N=0·5638	0·1620	0·1590	0·1180
+0·75 gm. N	NH_3-N=0·0027	0·0740	0·0640	0·0440
as Urea	NO_2-N=0·0037	0·0085	0·0490	0·0640

A perusal of the foregoing results shows that when urea is allowed to undergo slow oxidation on the soil surface a considerable amount of nitrogen undergoes loss. Urea in contact with soil surface is first converted into ammonium carbonate showing an increase in the ammoniacal nitrogen content of the system in the first part of the experiment and finally this ammoniacal nitrogen undergoes nitrification and is converted into nitrate nitrogen in the second part of the experiment. During this process of nitrification of urea on the soil surface there is always a possibility of formation and decomposition of an unstable intermediate product ammonium nitrite leading to loss of nitrogen according to the following equation :

$$NH_4NO_2 = N_2 + 2H_2O + 718 \text{ K. cals.}$$

Hence considerable amount of nitrogen is lost when urea undergoes nitrification on the soil surface. Thus when ammonium nitrite is formed in appreciable amounts, especially in acid soils, there is always a possibility of gaseous loss of nitrogen through its decomposition. Ghosh[6] has reported that the rate of decomposition of ammonium nitrite is more in presence of an acid. Losses of nitrogen due to formation and decomposition of ammonium nitrite have also been emphasised by Carter and Allison[7], Dhar[8], Wahhab and Uddin[9]. Soulides and Clark[10] obtained large losses of nitrogen following addition of 466 ppm of urea to several soils.

Another important point that has been brought out from the foregoing results is that amount of loss of nitrogen is different in different types of soils and greater the concentration of nitrogen added greater is the loss of nitrogen. The percentage losses of nitrogen on the application of urea from different types of soils are as follows :

TABLE V

Soil types	Concentration of N added as urea per 150 gm. of soil	Percentage loss of nitrogen After 20 days	After 40 days	After 60 days
(*a*) Ganga low land clay soil (Chinsurah, Dist-Hooghly)	1·50 gm.	3·6	29·8	64·5
	0·75 gm.	1·8	14·6	19·4
(*b*) Laterite sandy clay loam soil (Suri, Dist. Birbhum)	1·50 gm.	81·4	84·6	86·3
	0·75 gm.	65·2	67·8	72·5
(*c*) Ganga Riverine loam and clay loam soil (Berhampore, Dist. Murshidabad)	1·50 gm.	84·1	86·2	88·6
	0·75 gm.	71·3	71·8	79·1

The foregoing results show that (1) percentage loss of nitrogen is more in (*b*) and (*c*) types of soils than (*a*) type of soil, and (2) percentage loss of nitrogen in all the three types of soils is more with application of higher concentration of nitrogen and it increases with lapse of time.

Both ammonia and nitrous acid are constantly being formed in all moist soils on the application of urea. Due to high exchange capacity of (*a*) type of soil most of this ammonia is sorbed by the soil and may not be released readily to come into the solution phase and free to form ammonium nitrite, leading to loss of nitrogen. With higher concentration of urea there is always more ammonia formation which comes in the solution phase resulting more loss of nitrogen. This explains why percentage loss of nitrogen is more in (*b*) and (*c*) types of soils than (*a*) type of soil and it increasas with higher concentration of nitrogen added. Therefore, nitrogen loss seems to be more prominent in solution phase than in adsorbed condition. Again the tenacity with which cations are held by the soil complex is ordinarily in the following order :

$$Ca^{++} > Mg^{++} > K^{+} > NH_4^{+}$$

In the equiliberation process most of the nitrite ions may combine with cations other than NH_4^+ and form stable nitrites which slowly oxidise into nitrate. Loss of nitrogen, therefore, seems to be less in soils rich in cations other than NH_4^+ and high in cation exchange capacity. Loss of nitrogen due to formation and decomposition of ammonium nitrite on the application of nitrogenous compounds to soil therefore depends chiefly on pH, cation exchange capacity, kind and amount of other cations present in the soil complex. Such losses of nitrogen may partially be checked by making the soil favourable for rapid nitrate formation or by increasing its cation exchange capacity.

Summary

Loss of nitrogen during nitrification of urea has been studied in three different soil types of West Bengal. This loss of nitrogen has been explained due to formation and decomposition of an unstable intermediate product ammonium nitrite when urea undergoes nitrification in the soil surface. The percentage loss of nitrogen has been found to be more in Lateritic sandy clay loam soil and Ganga riverine loam and clay loam soil than in Ganga low land clay soil. Due to high exchange capacity of Ganga low land clay soil the ammonia formed is sorbed by the soil and may not be released readily to come into the solution phase and free to form ammonium nitrite leading to loss of nitrogen. Again in the equilibration process most of the nitrite ions may combine with cations other than ammonium and form stable nitrites which slowly oxidise into nitrate. Loss of nitrogen therefore seem to more prominent in solution phase than in sorbed condition and seems to be less in soils rich in cations other then ammonium and and high in cation exchange capacity.

References

1. Allison, F. E. *Advances in Agronomy*, **Vol. VII**, 213–50, 1955.
2. Lipman, J. G. and Blair, A. W. *Soil Science*, **12** : 1-19, 1921.
3. Russell, E. J. and Richards, E. H. *J. Agric. Sci.*, **8** : 495-563, 1917.
4. Russell, E. J. *Soil condition and plant growth* VI Ed. 360, 1932.
5. Dhar, N. R. and Ghosh, S. K. *Proc. Nat. Acad. Sci. India*, **24A (III)** : 219-224, 1955.
6. Ghosh, S. K. *Zeit. für Physikalische Chemie*, **206** : 321–326, 1957.
7. Carter, J. N. and Allison, F. E. *Soil Sci. Soc Amer. Pr* **25** : 484–486, 1961.
8. Dhar, N. R. *Intern. Congr. Chem. Fert.*, 1*st. Congr. Rome*, 1–65, 1938.
9. Wahhab, A. and Uddin, F. *Soil. Sci.*, **80** : 121–125, 1955.
10. Soulides, D. A. and Clark, F. E. *Soil Sci. Soc. Amer. Proc.* **22** : 308-311, 1958.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968

Effect of organic matter on phosphorus availability by maize

By

SANT SINGH *and* M. M. VERMA

College of Agriculture, Banaras Hindu University, Varanasi-5

Phosphorus is applied in the form of various fertilizers and manures, the availability of which amounts to only 10-30 per cent of quantity added to the soil (1). The remaining 70-90 per cent is consumed by micro-organisms, precipitated by soluble cations in the soil solution of plants. Several soil management practices have come to existence which directly or indirectly help in the release of phosphorus making the native and applied phosphorus in available forms. These are liming, application of organic matter, rate, time and frequency of fertilizer application, crop-rotation, cropping and erosion control practices, irrigation and drainage.

Out of all these management practices the addition of organic material is very promising. The phosphorus nutrition of plants is influenced in various ways by its application to the soil.

In view of the fact that less work has been reported regarding maize crop, which is one of the important cereals of India, the present investigation was undertaken with the object to find out the effect of organic matter on availability of phosphorus by this crop. Tonnage per acre may be highly increased by proper phosphorus application alone with organic matter.

Experimental

For pot experiment the soil was collected from 'Agricultural Farm' B. H. U. and was dried and well powdered to pass through 2 mm sieve. The experiment was conducted from June to October (1964-65). The big size cemented pots, having good drainage facility, were filled up with 50 lbs. of soil and following nutrient solutions were also added.

1. Ammonium sulphate at the rate of 60 lbs. N/acre.
2. Potassium sulphate at the rate of 60 lbs. K_2O/acre.
3. Manganese chloride at the rate of 20 lbs. Mn/acre.
4. Zinc sulphate at the rate of 25 lbs. Zn/acre.
5. Copper sulphate at the rate of 15 lbs. Cu/acre.
6. Borax at the rate of 5 lbs. Bo/acre.
7. $MgSO_4$ at the rate of 20 lbs. Mg/acre.
8. $FeSO_4$ at the rate of 10 lbs. Fe/acre.
9. Ammonium molybdate at the rate of 2 lbs. Mo/acre.

Nature of treatments:

(*i*) No. of fertilizers selected = 3
(Super phosphate, Bone meal, and ammonium phosphate)

(*ii*) No. of dose of fertilizers = 2
(40 lbs. of P_2O_5/acre and 80 lbs. of P_2O_5/acre)

(*iii*) No. of dose of F. Y. M. = 3
(10 tons, 20 tons and 40 tons/acre)

Total no. of treatments = 3 × 2 × 3 × 3+3 (Controls)
= 57

Soil Analysis

Loss on ignition	= 3·964
HCl (insoluble)	= 85·721
Sesquioxides	= 9·075
Fe_2O_3	= 3·985
Total P_2O_5	= 0·0794
Total CaO	= 0·9842
Total K_2O	= 0·946
Total MgO	= 0·5216
Total carbon	= 0·5738
Total nitrogen	= 0·0550
C : N ratio	= 10·4
pH	= 7·8

Phosphatic fertilizers :

	P_2O_5 content
1. Superphosphate	= 16 %
2. Ammonium phosphate	= 48 %
3. Bone meal	= 20·5 %

F. Y. M. analysis.

Total carbon	= 35·31 %
Total Nitrogen	= 0·949%
C : N ratio	= 37·56%

Results and Discussion

TABLE 1

Analysis of maize plants showing uptake of phosphorus at different levels of phosphatic fertilizers incorporated with 10 tons of F. Y. M. per acre after 75 days of growth

Pot No.	Treatment	Dry wt.	% P_2O_5	Total P_2O_5	Average/ pot	P_2O_5/acre
1	O_1S_1	27·8	0·24	66·72		
2	O_1S_1	28·4	0·27	76·68	71·24	6·31
3	O_1S_1	30·6	0·23	70·38		
4	O_1S_2	34·1	0·30	120·30		
5	O_1S_2	30·6	0·34	104·04	100·56	8·93
6	O_1S_2	29·8	0·32	95·36		
7	O_1A_1	28·5	0·25	71·25		
8	O_1A_1	30·2	0·27	81·54	76·66	6·37
9	O_1A_1	26·8	0·25	67·00		
10	O_1A_2	34·0	0·34	115·60		
11	O_1A_2	31·6	0·34	107·44	109·34	9·72
12	O_1A_2	30·5	0·30	105·00		
13	O_1B_1	27·5	0·20	55·0		
14	O_1B_1	29·7	0·22	63·43	57·57	5·13
15	O_1B_1	26·9	0·20	55·80		
16	O_1B_2	34·6	0·24	83·04		
17	O_1B_2	32·0	0·25	80·00	80·66	7·2
18	O_1B_2	32·9	0·24	78·96		
Control 1	O_0P_0	20·6	0·24	53·44		
Control 2	O_0P_0	23·1	0·21	48·51	48·99	4·40
Control 3	O_0P_0	21·4	0·21	44·94		

O_1 = F. Y. M. 10 tons per acre, O_0 = No F. Y. M.
S_1 = Superphosphate at 40 lbs. P_2O_5 per acre, P_0 = No P_2O_5
S_2 = Superphosphate at 80 lb. P_2O_5 per acre.
A_1 = Ammonium phosphate at 40 lbs. per acre.
A_2 = Ammonium phosphate at 80 lbs. P_2O_5 per acre.
B_1 = Bone meal at 40 lbs./acre.
B_2 = Bone meal at 80 lb./acre.

TABLE 2

Analysis of maize plants showing uptake of phosphorus at different levels of phosphatic fertilizer incorporated with 20 tons of F. Y. M. per acre after 75 days of growth

Pot No.	Treatment	Dry wt.	$\%P_2O_5$	Total P_2O_5	Average/ pot	P_2O_5/acre
19	O_2S_1	30·2	0·26	78·52	80·70	7·21
20	O_2S_1	29·2	0·28	83·44		
21	O_2S_1	27·6	0·29	80·04		
22	O_2S_2	35·2	0·30	105·60		
23	O_2S_2	37·0	0·33	122·10	115·66	10·27
24	O_2S_2	34·8	0·34	119·32		
25	O_2A_1	29·6	0·28	81·88		
26	O_2A_1	32·4	0·26	84·24	83·04	7·35
27	O_2A_1	30·0	0·28	84·00		
28	O_2A_2	38·4	0·35	134·40		
29	O_2A_2	36·5	0·34	123·90	123·98	11·02
30	O_2A_2	35·7	0·32	113·64		
31	O_2B_1	26·4	0·24	58·56		
32	O_2B_1	27·4	0·25	68·50	60·19	5·43
33	O_2B_1	24·2	0·22	53·52		
34	O_2B_2	29·2	0·32	93·44		
35	O_2B_2	27·8	0·30	83·40	89·09	8·00
36	O_2B_2	26·6	0·34	90·44		
Control 1	O_0P_0	20·6	0·24	53·44		
Control 2	O_0P_0	23·1	0·21	48·51	48·99	4·40
Control 3	O_0P_0	21·4	0·21	44·94		

TABLE 3

Analysis of maize plants showing uptake of phosphorus at different levels of phosphatic fertilizers incorporated with 40 tons of F. Y. M. per acre after 25 days of growth

Pot No.	Treatment	Dry wt.	% P_2O_5	Total P_2O_5	Average/ pot	P_2O_5/acre
37	O_3S_1	30·8	0·29	79·32		
38	O_3S_1	31·9	0·28	89·32	97·78	7·80
39	O_3S_1	31·5	0·30	94·50		
40	O_3S_2	36·4	0·34	123·76		
41	O_3S_2	37·8	0·35	122·30	121·68	10·08
42	O_3S_2	35·0	0·34	119·00		
43	O_3A_1	32·0	0·26	83·20		
44	O_3A_1	34·6	0·25	86·50	87·56	7·78
45	O_3A_1	31·0	0·30	93·00		
46	O_3A_2	40·4	0·35	141·40		
47	O_3A_2	38·6	0·37	142·82	136·10	12·54
48	O_3A_2	36·5	0·34	124·10		
49	O_3B_1	28·4	0·23	65·32		
50	O_3B_1	27·3	0·24	65·52	64·78	5·75
51	O_3B_1	25·4	0·25	63·00		
52	O_3B_2	36·4	0·32	116·48		
53	O_3B_2	32·4	0·30	97·20	98·56	4·46
54	O_3B_2	30·4	0·27	82·02		
Control 1	O_0P_0	20·6	0·24	53·44		
Control 2	O_0P_0	23·1	0·21	48·51	48·99	4·40
Control 3	O_0P_0	21·4	0·21	44·94		

TABLE 4

Analysis of residual soils for available phosphorus after the harvest of the maize plants on 10 tons of F. Y. M. application

S. N.	Treatment	$\%P_2O_5$	Total P/in gm (%)	Available P/acre
1	O_1S_1	0·016	0·364	32·00
2	O_1S_2	0·028	0·637	56·00
3	O_1A_1	0·018	0·4094	36·00
4	O_1A_2	0·030	0·6285	60·00
5	O_1B_1	0·012	0·273	24·00
6	O_1B_2	0·020	0·455	40·00
7	O_0P_0	0·008	0·182	16·0

TABLE 5

Analysis of residual soils for available phosphorus after the harvest of the maize plants on 20 tons of F. Y. M. application

S. N.	Treatment	$\%\ P_2O_5$	Total P/in gm	Available P/acre
1	O_2S_1	0·017	0·3867	34·0
2	O_2S_2	0·028	0·6461	57·6
3	O_2A_1	0·018	0·3931	37·2
4	O_2A_2	0·032	0·7280	64·0
5	O_2B_2	0·013	0·2957	26·0
6	O_2B_2	0·024	0·5232	48·0
7	O_0P_0	0·07	0·1774	15·6

TABLE 6

Analysis of residual soils for available phosphorus after the harvest of the maize plants on 40 tons of F. Y. M. application

S. N.	Treatment	$\%P_2O_5$	Total P/in gm (%)	Available P/acre
1	O_3S_1	0·018	0·4095	36·0
2	O_3S_2	0·029	0·6043	54·4
3	O_3A_1	0·019	0·4340	38·2
4	O_3A_2	0·032	0·7472	65·6
5	O_3B_1	0·013	0·3048	26·8
6	O_3B_2	0·024	0·5551	49·0
7	O_0P_0	0·007	0·1683	14·8

A perusal of data shows that available phosphorus increases with increase in organic matter levels. On 80 lbs of P_2O_5 application phosphorus availability was higher as compared to 40 lbs of P_2O_5. The various phosphatic fertilizers are also noticed to affect the available phosphorus content of the experimented soils. The order of efficiency for phosphatic fertilizers is found to be as ammonium phosphate > superphosphate > Bone meal.

Addition of organic materials resulted in the increased dry matter of the plants. It may be partly due to a greater availability of phosphorus to plants. F. Y. M. having a wide C/N ratio about 37·5 disturbed the C/N ratio of the soils. Dhar and Ghildyal (2) also reported that due to slow oxidation under sterile conditions C/N did not decrease much, but under unsterile conditions the ratio decreased to 21. In moist condition farm yard manure contains about 406 lbs of phosphorus per ton which may be expected to be available to certain extent to the plants. (Mc Auliffe *et al*, 3, 4). Many workers (5, 6, 7, 8) have established that phosphates when incorported with organic materials are readily available to plants. The chief reason is that the organic matter decomposes to give carbonic acid which convert insoluble calcium phosphates into soluble forms. Struther and Sieling (9) and Truog (10) have also reported that certain organic substances are effective in preventing the precipitation of phosphorus by iron and aluminium. Generally citric, oxalic, tartaric and lactic acids are formed during the decomposition of organic matter which are also helpful in making phosphate available. Dhar *et at* (11, 12, 13) have also suggested that a mixture of organic substances like F. Y. M., straw, plant leaves, grass etc., fortified by addition of calcium phosphate prove to be of immense value in building up soil fertility permanently by decreasing acidity, fixing atmospheric nitrogen and also supplying available phosphate, potash and trace elements.

Table Nos 4, 5, 6 entailing the analyses of pot soils after the harvest of maize increase available phosphorus with increasing organic matter doses.

Summary

Results indicated that the yield of dry matter and uptake of phosphorus by maize was greatly affected by the higher dose of phosphates along with maximum dose of F. Y. M. The availability of soil-phosphorus after harvesting the crop also increased with increased application of farm yard manure. Several inorganic phosphatic fertilizers *viz.*, super phosphate, ammonium phosphate and bone meal containing total P_2O_5 to the extent of 16 %, 48 % and 20·5 % respectively, were applied at the rate of 40 lbs and 80 lbs P_2O_5 per acre. It was noticed in this experiment that 80 lbs of P_2O_5 incorporated with 40 tons of F. Y. M. per acre was more effective in increasing the available P_2O_5 and total crop yield than the dose of 40 lbs of P_2O_5 with 40 tons of F. Y. M. per acre for maize crop. All the results with 40 lbs and 80 lbs of P_2O_5 incorporated with 10, 20 and 40 tons of F. Y. M. per acre were yielding significant data over control.

Thus it may be concluded that the increasc in total uptake of phosphorus in plants with increasing organic matter may be due to :

(1) Some phosphorus being supplied by F. Y. M. itself to the growing plants.

(2) F. Y. M. helping the release of more native phosphorus for use of plants and reducing fixation of applied phosphorus.

References

Russell, E. J. Soil conditions and Plant-growth, pp. 36, 1950.

Dhar, N. R. and Ghildyal, B. N. P. A study of composting of cowdung under sterile and unsterile conditions. *Proc. Nat. Acad. Sci. India*, 20–34, 1951.

Mc Auliffe, C. D., Hall, N. S., Dean, L. A. and Hendricks, S. P. *Soil Sci. Soc. American proceedings*, **11** : 119–123, 1947.

Mc Auliffe *et al.* Utilization of phosphorus by plants in Farm manures. *Soil. Sci.*, **68** : 185, 1949.

Rahn, E. M. *Proc. Amer. Soc. Hort. Sci.*, **37** : 713–7, 1939.

Hester, J. B. and Shelton, F. A. *Va. Truck. Exp. Sta. Bull.*, **94** : 1397-428, 1937.

Metzger, W. H. *Soil. Sci.*, **32** : 513–26, 1940.

Aslander, A. *Trans. 4th International Confr. Soil Sci.*, 2, 1953.

Stuthers, P. H. and Sieling, D. H. *Soil Sci.*, **69** : 205, 1950.

Truog, E. *Soil. Sci. Amer. Proc.*, **11** : 305–308, 1946.

Dhar, N. R. and Ghosh, S. K. *Proc. Nat. Acad. Sci. India*, **24** : 201-217, 1954.

Dhar, N. R. and Nagpal, K. L. *Nat. Acad. Sci. India*, **24** : 231–235, 1954.

Dhar, N. R. and Pal, S. K. *Proc. Nat. Acad. Sci. India*, **25** (4) : 467, 1956.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968.

Some aspects of the influence of humic substances on soil microflora

By

A. C. GAUR, R. S. MATHUR *and* K. K. R. BHARDWAJ

Division of Microbiology, I. A. R. I., New Delhi

Introduction

The organic fraction of soil consists of a complex system of various substances which according to the recent concepts of soil organic matter can be divided into two groups (*i*) Non-humic substances and (*ii*) humic substances. The former consists of all classes of organic compounds *e.g.* carbohydrates, proteins, fats etc. and latter are represented by humin, humic, fulvic and hymatomelanic acids. They are high molecular weight, coloured and colloidal substances which are synthesized during the decomposition process through the reactions of decomposition and synthesis.

Humic acid represents one of the important fractions of humic substances and has received more attention than the other fractions. This fraction is soluble in alkalies and neutral salts and precipitated by acids. Humic acids are probably formed during the condensation of aromatic compounds with amino acids or peptides with the possible participation of reducing substances (16). They are known to exert beneficial effect on the growth and developement of plants (6, 11, 12, 15, 21, 26).

Although there is no agreement as regards the beneficial effects of humic acid on the microorganisms, there is a reason to believe that humic acids like many other organic substances represents a potential source of energy and mineral nutrients for various types of microorganisms which are capable of decomposing them.

Nikitin (20) reported the decomposition of humic acid by *Pseudomonas fluorescens* and Schonwalder (25) showed that some *Micrococcus* species, *Corynebacterium* and certain yeasts decompose humic acid. Burges and Latter (4) reported decomposition of humic acid by a large number of fungi. Flaig and Schmidt(9) described humic acid as a good source of carbon for *Penicillium* and Gerretson (13) found that in the presence of small amount of humic acid the growth of *Aspergillus niger* was increased upto 40 percent over control. On the other hand Lal and Mazumdar (18) denied the utilization of α-humus by *Aspergillus* and *Penicillium* species and out of 150 species of pure cultures of various actinomycetes detected by Fedorov and Iliana (8), only a few were reported to use humic acid as the sole source of carbon and nitrogen. Kuster (17) and Flaig and Schmidt (9) could not detect a stimulating effect of humic acids on a large number of microorganisms and Rybalkina (22) reported toxicity of humic acid to the growth of *Clostridium pasteurianum*.

Where some workers (1, 3, 8, 9, 12, 13, 17, 22) have reported positive or negative effect of humic acids on the growth of certain bacteria, fungi, and actinomycetes, few have reported the stimulating action of natural humus compounds(27)

on the nitrogen fixation by aerobic nitrogen fixers. There seems to be no agreement as regards the beneficial effect of humic acid on the growth of soil microorganisms. The purpose of the experiments reported here was to investigate the effect of humic acid or sodium humate on the growth and nitrogen fixing power of *Azotobacter chroococcum* and *Rhizobium trifolii*.

Material and Methods

The humic acid used in the experiment was extracted from soil and farmyard manure by Chaminade's method (5). Humic material from soil or manure was extracted with 3 per cent ammonium oxalate solution in the ratio of 1:5 and extraction was continued for 24 hours with frequent shaking. The extract was filtered and filtrate was brought to pH2 by the addition of hydrochloric acid to precipitate humic acid fraction. Humic acid was filtered and washing with distilled water was continued until free of oxalate and Chloride ions. Later humic acids from both the sources were dialysed against distilled water to get the humic acid free of oxalate and other ions.

Sodium humate was prepared from humic acid by neutralising the acid with N/10 NaOH. The humate was also dialysed to remove the sodium ions, if any.

Jensen's liquid medium (14) was used for the growth and nitrogen fixing power of *Azotobacter* and for the study on the growth of *Rhizobium trifolii*, yeast extract mannitol broth (10) was used. The composition of the media is as follows :

Jensen's medium		Y. E. M. medium	
Sucrose	. . 20 gm.	Mannitol	. . 10 gm.
K_2HPO_4	. . 1·0 gm.	K_2HPO_4	. . 0·5 gm.
$MgSO_4 . 7H_2O$	. . 0·5 gm.	$MgSO_4 . 7H_2O$	. . 0·2 gm.
NaCl	. . 0·5 gm.	NaCl	. . 0·1 gm.
$FeSO_4$	. . 0·1 gm.	$CaCO_3$	. . 3 gm.
Na_2MoO_4	. . ·005 gm.	Yeast Extract	. . 1 gm.
Agar	. . 1 gm.	Water	. . 1 litre.
Water	. . 1 litre.		

50 ml. of media were used for the growth and nitrogen fixation studies by the organisms concerned. Different quantities of humic acid or sodium humate were added to the media, sterilized at 15 lb pressure for 20 minutes, inoculated with the respective organisms and were incubated at 30°C for 21 days for nitrogen fixation and 14 days for growth studies. Nitrogen fixation was studied with *Azotobacter chroococcum* under laboratory conditions. Other experimental conditions remained the same in all cases. Each treatment was quadruplicated. The amount of nitrogen fixed was estimated by micro-kjeldahl method and the growth of the organiam was determined turbidimetrically by using Klett-Summerson photoelectric colorimeter employing red filter of the wave length of 660 mμ. The optical density was calculated from the following relationship.

$$\text{Colorimetric reading} = \frac{1000 \times \text{O. D.}}{2}$$

In the plot culture experiment the effect of sodium humate from farmyard manure was investigated on tetraploid berseem crop (*Trifolium alexandrinum*).

The seeds were inoculated with fresh culture of *Rhizobium trifolii* and were sown in unsterilized soil to which 0·005% sodium humate and 0·017% farmyard manure at the rate of 6 lbs. nitrogen in each case were added. Each treatment was quadruplicated. The crop was harvested in four cuttings and dry weights of the cuttings were recorded.

Results

TABLE 1

Influence of humic acid on nitrogen fixation by Azotobacter chroococcum (strain 41)

Treatment	mg. N fixed/50 ml. medium (Average of 4 replications)	% increase over control
Control	17·17	—
1 mg. humic acid	20·44	19·04
3 mg. humic acid	19·64	14·3
5 mg. humic acid	20·12	17·1
10 mg. humic acid	21·35	24·3
Significant at 1% level	C. D. at 1% = 1·716.	

TABLE 2

Influence of sodium humate on nitrogen fixation by Azotobacter chroococcum (strain 41)

Treatment	mg. N fixed 50 ml. medium (Average of four replications)	% increase over control
Control	14·70	—
5 mg. sodium humate	16·60	12·9
10 mg. sodium humate	15·82	7·9
15 mg. sodium humate	16·87	14·6
20 mg. sodium humate	16·50	12·2
25 mg. sodium humate	16·89	14·9
Significant at 1% level	C. D. at 1% = 0·614.	

TABLE 3

Influence of humic acid on nitrogen fixation by 3 different strains of Azotobacter chroococcum

Treatment	mg. N fixed/50 ml. (average of four replications)	% increase over control
Control (Russian)	19·60	—
Control (Samalkot strain)	18·55	—
Control (Cuttack strain)	17·08	—
5 mg. humic acid (Russian strain)	21·77	11·0
5 mg. humic acid (Samalkot strain)	20·72	11·0
5 mg. humic acid (Cuttack strain)	19·32	13·1
Significant at 5%	C. D. at 5% = 0·956	

TABLE 4

Influence of humic acid on growth of Azotobacter chroococcum (Russian strain)

Treatment	Growth (Optical Density) after 5 days	9 days	14 days	Total	% increase over control
Control	0·0056	0·0334	0·0353	0·0743	--
1 mg. humic acid	0 0073	0·0373	0·0403	0·0849	14·5
3 mg. humic acid	0·0076	0·0376	0·0443	0·0895	20·64
5 mg. humic acid	0·0096	0·0434	0·0476	0·1006	35·62
Significant at 5% level				C. D. 5% = 0·0140	

TABLE 5

Influence of humic acid on the growth of Rhizobium trifolii

Treatment	Growth (Optical Density) after 5 days	10 days	15 days	Total growth	% increase over contro
Control	0·0454	0·0720	0·0823	0·1997	--
5 mg. humic acid	0·0713	0·1040	0·1213	0·2966	48·50
8 mg. humic acid	0·0787	0·1073	0·1334	0·3194	59·43
10 mg. humic acid	0·0830	0·1400	0·1994	0·4224	111·40
Significant at 1% level				C. D. at 1% = 0·023. C. D. at 5% = 0·016.	

TABLE 6

Influence of sodium humate and farmyard manure on the yield of berseem inoculated with Rhizobium trifolii

Treatment	Dry weight of cuttings (gm.) 1st cutting	2nd cutting	3rd cutting	4th cutting	Total yield	% increase over control
Control	0·475	1·450	2·770	3·420	8·110	—
Inoculated with *Rhizobium*	0·400	1·570	2·870	3·920	8·96	10·0
Inoculated with *Rhizodium* + 0·005% sodium humate	0·425	1·660	3·550	4·370	10·00	23·3
Inoculated with *Rhizobium* + 0·017% farmyard manure	0·450	1·560	2·92	4·300	9·23	13·8

Discussion

The foregoing results show that both symbiotic and non-symbiotic nitrogen fixers studied have responded positively to the application of humic acid or sodium humate under laboratory conditions. In pot culture experiments inoculation of seeds with *Rhizobium trifolii* in presence of 0·005% sodium humate in the soil increased the yield of berseem crop appreciably.

Although some workers (9, 17) have denied the positive effect of humic acids on the growth of some groups of microorganisms and indications are there (22) where humic acid has proved toxic to certain microorganism (*Clostridium pasteurianum*), the present studies have not detected the negative effect of humic substances on the microorganisms studied.

In all the experiments carried out in this connection, significant increases in growth and nitrogen fixation by the organisms tested, have been observed under cultural conditions. The growth of *Azotobacter chroococcum* (Russian strain) and *Rhizobium trifolii* (tables 4 and 5 respectively) increased appreciably due to addition of humic acids extracted from a soil to their respective culture media. The increase in the growth of Azotobacter and Rhizobium varied from 14 to 35 percent and 48 to 111 percent respectively with different quantities of humic acid added.

The quantities of nitrogen fixed by *Azotobacter* are significantly enhanced in presence of humic acid or sodium humate although the amounts of nitrogen fixed are not proportional to the increasing doses of humic acid or sodium humate (tables 1 and 2). However, there is no negative effect on the activity of the organism tested with higher quantities of sodium humate or humic acid applied. Humic acid from farmyard manure proved more effective in nitrogen fixation than its sodium humate. The present studies in no way prompt one to explain the greater effectiveness of humic acid or sodium humate, it can be assumed that humic acid causes more stimulation due to certain peculiarities which may be altered by the alkali used for the preparation. This inference can be drawn from the statement of Russell (23) who has pointed out that treatment of humus with strong alkalies causes some chemical alterations in the humic acid extracted.

The stimulative effect of humic acid on nitrogen fixation by these different strains of *Azotobacter* (table 3) further confirmed the above findings that humic acid affects the activity of this organisms.

The effect of humic acid on the growth of *Rhizobium trifolii* was confirmed in pot culture studies. There has been appreciable increase in the yield of tetraploid berseem crop when inoculated with this organisms in presence of 0·005% sodium humate. The increase with farmyard manure is comparatively very much less although the quantity of nitrogen in both the materials was the same. Apparently, this effect is not due to nitrogen content of the sodium humate.

Sodium humate might have exerted its direct influence on the plants as pointed by various workers (6, 11, 12, 15, 21, 26) but its stimulative action on the growth of *Rhizobium trifolii* observed in the laboratory may be one of the causes of the increase in yield of the crop. Bhardwaj and Gaur (2) had similar experience with diploid berseem where the yield of the crop was increased from 5 to 12% due to inoculation of berseem seeds with specific *Rhizobium* in presence of 0·04% added sodium humate to the soil. The authors also observed a very favourable effect of calcium humate on the nodulation and yield of pea (*Pisum sativum*) in sand culture. In both the crops the yield, nitrogen content and uptake by the crop were appreciably increased over the control.

This positive effect of humic acid on the growth of *Azotobacter* and *Rhizobium* has been ascribed to the presence of certain substances in humic acids. Some have attributed this effect to the presence of iron in humic acid (3) while others (19, 24) report chelation of mineral elements by humic acids. These chelated elements are reported to be made available easily to plants and microorganisms and thus the growth is favourably affected.

If iron is a part of humic acid molecule, the stimulation may not be due to its iron content because it is well known that *Azotobacter* or *Rhizobium* are incapable of decomposing humic acids. At the same time the direct effect of humic acids on growth of plants and microorganisms may not be ruled out.

Summary

Some workers have reported that humic acids can be decomposed by some bacteria and fungi and positive and negative effects of this substance on the growth of some organisms have been observed by other workers as well. However, there seems to be no agreement as regards the beneficial effect of humic acids on soil microflora.

Our results show that humic acid or sodium humate from soil or farmyard manure, both increase the growth and nitrogen fixing capacity of *Azotobacter chroococcum*.

The substantial increases in the growth of *Rhizobium trifolii* under cultural conditions in presence of humic acid were observed. In a pot culture experiment yield of berseem (*Trifolium alexandrinum*) was increased appreciably due to the inoculation with specific *Rhizobium* when 0·005% sodium humate was also added to the soil.

References

1. Allison, F. E. and Hoover, S. R. The response of rhizobia to natural humic acid. *Soil Science*, **41** : 333-340, 1936.
2. Bhardwaj, K. K. R. and Gaur, A. C. Humic acid in relation to bacterial inoculation of crops. *Agrochimica*, **12** : 100–108, 1968.
3. Burk, D, Line-weaver, H. and Horner, C. K. Iron in relation to stimulation of growth by humic acids. *Soil Science*, **33** : 413-433, 1932.
4. Burges, A. and Latter, P. Decomposition of humic acids by fungi. *Nature*, **186** : 404–405, 1960.
5. Chaminade, R. A method of determination of humus from soils. *Ann. Agron.*, **16** : 117-132, 1946.
6. Chaminade, R. The effect of humic acid on the growth of plants and their nutrition. *6th Intern, cong. soil science*, **D** : 443–448, 1956.
7. Dyakonova, K. V. Iron humus complexes and their role in plant nutrition. *Pochvovedenie*, No. 7, 19–25, 1962.
8. Fedorov, M. V. and Iliana, T. K. Utilization of humic acid by soil actinomycetes as a sole source of carbon and nitrogen. *Microbiologiya*, **32** : 272–276, 1963.
9. Flaig, W. and Schmidt, H. L. The effect of humic acid on several *Penicillium* species. *Arch Microbiol*, **27** : 1–32, 1957.

10. Fred, E. B. and Waksman, S. A. Laboratory manual of General Microbiology. *McGraw Hill Book Company Inc. New York.* 370. *Seventh Avenue, Medium,* No 79, 1928.

11. Gaur, A. C. Influence of humic acid on growth and mineral nutrition of plants. *Bull. Ass. Franc. Sol,* No. 5 : 207-219, 1964.

12. Gaur, A. C. and Mathur, R. S. Effect of sodium humate on the yield and nitrogen content of *Lolium perenne. Proc. Nat. Acad. Sci. India* **36**A : 879-882, 1966.

13. Gerretson, F. C. The application of Aspergillus method for the practical determination of potassium and phosphate in soil samples. *Abs. in Proc. 4th Intern. cong. Microbiol,* 487-488, 1949.

14. Jensen, H. L. Notes on the biology of *Azotobacter. Proc. Soc. Appl. Bacterial.,* **14** : 89-94, 1951.

15. Khristeva, L. A. Participation of humic acid and other organic substances in the nutrition of higher plants. *Pochvovedenie,* No. **10** : 46-59, 1953.

16. Kononova, M. M. Soil organic matter. *Pergamon Press, Oxford, London, New York, Paris,* 1961.

17. Kuster, E. Abbay heterocyclisation N-verbin-dungen durch verschiedene Boden mikroorganismen. *Zbl. Bakt. I. orig.,* **159** : 350, 1952.

18. Lal, A. and Mazumdar, S. K. Microbiological studies, Interrelation between humus, microorganic flora, mineral ingradients and growth. *Proc. Nat. Acad. Sci. India,* **23** : 115-136, 1953.

19. Mortensen, J. L. Complexing of metals by soil organic matter. *Proc. Soil Sci. Soc. Amer.,* **27** : 11-19, 1963.

20. Nikitin, D. I. Decomposition of soil humic acid by microorganism. *Izv. Akad. Nauk. Ser. Biol.,* **4** : 618-625, 1960, (quoted from soils and Fert., **23** : 416, 1960).

21. Prat, S. On permeability and effect of humus substances on plant cells. *5th Intern. congr. Biochem., Moscow,* 1961.

22. Rybalkina, A. V. Effect of humic acid on development of *Clostridium. Trudy. Inst. MiKrobiol. Akad. Nauk.,* **5** : 136-149, 1958.

23. Russell, E. W. Soil conditions and plant Growth. *Longmans, Green and Co. London.*

24. Schnitzer, M. and Skinner, S. I. M. Organometallic interactions in soils. *Soil Sci.,* **96** : 86-93, 1963.

25. Schonwalder, H. The utilization of humic acids as a food source by microorganisms. *Arch. Microbiol.,* **30** : 162-180, 1958. (Soils and Fert., **21** : 284, 1958).

26. Smidova, M. The influence of humic acid on respiration of plants. *Biol. Plant,* **2** : 152-164, 1960.

27. Waksman, S A. and Iyer, K. R. M. Contribution to our knowledge of chemical nature and origin of humus II. The influence of synthesized humus compounds and natural humus on soil Microbiologica' process. *Soil Science,* **34** : 71-82, 1932.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968

Green house studies on the utilization of weed as a source of organic matter under well-drained and submerged conditions

By

G. C. SHUKLA *and* O. P. VIMAL

Division of Soil Science and Agricultural Chemistry Indian Agricultural Research Institute, New Delhi-12

The role of organic matter in improving the physicochemical and biological properties of the soil is well known. When the organic matter is allowed to decompose in the soil, it adds the major constituent elaments, *e.g.* C, N, P, K, Ca and S and minor-- Cu, Zn, Mo, Mn, Fe, B, Cu and Mo to the soil. Moreover, in the presence of organic matter, the native plant nutrients present in the soil are made available. The humus content of the soil increases. Many organic compounds liberated in the soil as a result of the breakdown of organic matter have an ameliorating action on soil pH. These also bear growth promoting properties. Physical properties of the soil, like, water-stable-aggregates, water-holding capacity, tillh, porosity and sticky point are improved. The microflora and the microfauna of the soil grows rapidly. A number of reviews covering the many sided aspects of soil organic matter have been published in the last two decades (Bremner [4-5], Broadbent [6-7], Deuel *et al*[9], Dubach and Mehta[13], Dubach *et al*[14], Flaig[16], Fuller[18], Kononova[21], Mortensen[23], Nagar and Dutta[25], Scheffer and Ulrich[32], Whitehead[38], and Zenobius[40]). In India, significant contribution has been made in this field by Dhar and co-workers[10,11].

On account of these beneficial effects of organic matter, an endeavour is made by the soil scientists and agronomists, all over the world, to direct all available and possible crop residues to the fields.

The weed-plants are generally known for their association with harmful effects in crop growth. These plants are rich in major and minor elements. The biological constants : C/N, C/P and N/P ratios of many of them are narrow. These properties lend the weeds highly suitable for direct application to the fields as an organic manure. The usefulness of the weeds in enhancing the soil fertility has been stressed by Pieters[28], Sprague[35], Spaulding and Eisenmenger[34], Singh and Singh[33], Prashad and Dange[31], and Nagar[24]. Basu and Sirur[2] who studied the effect of Patata shevna, a common leguminous weed on the yield of sugarcane reported it to be significantly superior to all other green manures. Miller and Turk[22] also stressed the importance of turning weeds as a green manure in tobacco plantations. Bear[3] discussed the role of weeds as a source of organic matter in the improvement of soil structure, control of soil erosion and the availability of plant nutrients.

The present paper interprets and records the investigations undertaken to study the effect of some commonly available weeds, as a source of organic matter, in the yield and nutrient uptake of nitrogen, phosphorus and potassium by wheat and paddy. These two important crops were selected for the study because one grows under the aerobic and the other in the anacrobic condition of the soil. The chemistry and the biology of the soil varies greatly under these two conditions.

Materials and Methods

(*a*) *Preparation of soil* : Surface soil, 0–9″ (0-22·5 cms.), was collected from the main block of the agronomy division farm, I. A. R. I., New Delhi. The soil was air dried and passed through 1/4″ (6·3 mm.) screen for use in pot-culture experiments. The soil was screened through 2 mm. sieve and then dried at 105°C for chemical analysis. The physico-chemical properties of the soil used for pot-culture experiment are given in table I.

TABLE 1

Soil – analysis

pH (1 : 2·5)	8·05
Conductivity (m.mhos/cm. at 25°C 1 : 2·5)	0·70
Maximum water-holding capacity %	33·81
Mechanical analysis	
Sand %	71·85
Silt %	6·69
Clay %	18·65
Textural Class	Sandy clay loam
Total nitrogen %	0·065
Organic carbon %	0·561
C : N ratio	8·62
Available nitrogen	203·3 kg/ha
Available phosphorus	20·6 kg/ha
Available potassium	186·5 kg/ha

(*b*) *Preparation of weeds* : The shoots of seven commonly available weeds, belonging to six different families, were collected from the agronomy division farm. They were first air dried and then grounded in a Willey crushing machine to pass through 2 mm. sieve. Botanical description of the weeds is mentioned in table II.

TABLE II

Botanical description of the weeds

Botanical name	Family	Common English (E), Hindi (H), and Punjabi (P) names
1. *Trianthema monogyna*	Aizoaccae	Santhi, Patherchata (H)
2. *Lantana camara*	Verbenaceae	Phul lakari (P)
3. *Heliotropium eichwaldii*	Borgianacea	Uttahchara (H)
4. *Croton sparsiflorus*	Euphorbiaceae	Ban-mircha (H)
5. *Cannabis sativa*	Cannabinacea	Bhang (H & P)
6. *Xanthium strumarium*	Compositae	Cockle-bur (E), Ban-okra (H)
7. *Carthamus oxyacantha*	Compositae	Pohli (P), Kantiari (H)

These weeds were at first dried in an oven at 105°C and then chemically analysed. The results are reported in table III.

TABLE III

Chemical analysis of weeds

Chemical constituents	T. monogyna	L. camara	H. eichwaldii	C. sparsiflorus	C. sativa	X. strumarium	C. oxyacantha
Org. C %	42·50	48·10	47·18	41·50	38·60	46·70	43·28
Total N %	2·06	1·62	2·46	3·10	3·28	2·82	1·28
Total P_2O_5%	1·55	0·92	1 63	1·53	1·21	1·13	0·83
Total K_2O%	2·12	1·21	1·79	1·58	1·70	2·42	1·12
CaO %	2·48	3·66	2·22	1·84	2·18	3·15	3·54
C : N	20·63	29·69	19·17	12·65	11·76	16·56	33·81
C : P	42·18	52·20	28·92	27·12	32·12	47·26	51·82
Fe (ppm)	173·56	262·24	156·63	187·18	162·45	296·32	168·98
Zu (,,)	51·25	49·62	47·06	41·35	43·72	52·14	42·30
Cu (,,)	10·28	8·92	9·14	11·46	12·74	9·51	8·46
Ether extract %	6·12	5·71	4·47	5·19	4·81	5·28	4·20
Carbohydrates %	38·22	33 60	35·31	32·38	24·90	31·56	37·80
Hemi-Celluloses %	8·28	9·30	6·03	10·42	14·28	6·96	11·00
Celluloses %	9·14	10·10	13·25	12·05	13·40	12·28	12·21
Lignin %	13·32	13·48	12·35	9·27	6·20	12·48	13·84
Proteins %	12·87	10·12	15·37	19·38	20·50	17·62	8·00

(*c*) *Green-house experiments (wheat and paddy crops)* : For wheat 10 lbs. and for paddy 20 lbs. soil was taken in the 24 earthen pots required for raising each crop. These included eight treatments, and three replications. The eight treatments consisted of one control set and the seven sets in which the seven weeds, listed in table II and prepared as given in (*b*) above, were added the soil at 2% of the soil weight. After the addition of the weeds to the soil, these were allowed to decompose for one month at 50% moisture holding capacity before transplanting paddy-seedlings or, sowing wheat-seeds. In case of paddy, ten seedlings of the variety Taichung native - 1 were transplanted on June 11, 1965. In others, ten seeds of wheat, variety N. P. 824, were sown on December 17, 1965. After one week of sowing or transplanting, only five plants were retained in each pot. Submerged conditions were maintained for the growth of paddy crop with 1" (2·54 cms.) layer of the water above the soil surface. Wheat crop was grown under well-drained conditions. Dry matter yield obtained from both the crops was stored separately for grain and straw. This was used for yield data and plant analysis after drying in an oven at 105°C.

(*d*) *Methods of analysis* : Organic carbon, total nitrogen, pH, conductivity, and water holding capacity were determined according to the methods described by Jackson[20] Available nitrogen was estimated by the procedure of Subbiah and Asija[36]. Available phosphorus was extracted by Olsen's extractant (Olsen[26]) and determined colorimetrically by the method of Dickman and Bray[12]. Hanway

and Heidal's[19] method was used for the determination of available potassium. Iron, Zinc and Copper were estimated as discussed by Chapman and Pratt[8]. Plant analysis in respect of inorganic constituents was done according to Piper[30]. Ether extract was estimated by extraction in a soxhlet apparatus. Crude protein was obtained, multiplying total nitrogen by the factor of 6·25. Hemicelluloses, celluloses and lignin were determined by the method of Fred and Waksman[17]. Soluble carbohydrates were found by difference.

Results and Discussions

The data presented in table IV*a* and *b* indicates that all the seven weeds added to the soil under submerged conditions had a significant effect on dry matter yield as well as nutrient uptake with regard to nitrogen, phosphorus and potassium. Similar results were obtained, under well drained conditions, with all the weeds, but two, namely *L. camar* and *C. oxyacantha*. The dry matter yield as well as nutrient uptake with respect to these two weeds was significantly low. This depression in yield observed with the above two weeds may be due to their slow rate of decomposition. In incubation experiments, made under similar conditions, it was observed that *L. camara* and *C. oxyacantha* with C : N ratios as 29·69, 33·81 and lignin percent as 13·48, 13·84 caused an initial immobilisation of available nitrogen (data unpublished). It is important to note here, that, the C : N ratios as well as the lignin content of other weeds are low. Pink[29] expressed the limit for C/N ratio, around 20, for efficient mineralisation of soil nitrogen. Above this, immobilisation is likely to occur due to imbalance of energy and protein requirement of micro-organisms to build up their protoplasm. Peevy and Norman[27] stated, that, lignin content is an important factor controlling the release of nutrients for plant growth. The materials having a wide C : N ratio, cause an initial immobilisation of nitrogen, has been reported by Ferguson[15], Winsor and Pollard[39], and Vimal[37].

It is interesting to record that whereas there was a depression in yield with the above two weeds, under well drained conditions, no such adverse effect was noted under submerged conditions. On the contrary, there was an increase both in the yield of grain and straw on the addition of these two weeds. This anomalous behaviour of the same substrate, under the two different environmental conditions, may be due to bio-chemical heterogenity of the microflora, subsisting under the two conditions. Under well drained conditions, nitrification is accomplished by highly specific, aerobic, autotrophic bacteria, while the ammonification process under the submerged conditions is associated with the general purpose, heterotrophic micro-organisms, functioning at a low energy level.

The beneficial effect of the weeds, in general, as observed in increased nutrient uptake and dry matter yield is related to the supply of available nitrogen at the requisite stage of the growth of the plants. It has been reported (annonymous)[1] that the greatest uptake of nutrients N and P_2O_5 takes place between 14th and 17th day after transplantation of paddy seedlings and there is no uptake of nutrient after the flowering. Incubation experiments conducted in the laboratory with the above weeds, under similar conditions, showed that maximum availability of nutrients (N, P and K) is observed before 40 days. The supply being compatible at the time of the demand. Besides this, the addition of weeds enhanced the soil fertility through an increase of organic carbon, exchangeable bases and humic acid content as observed at 120 days (data unpublished). Data in table III shows that these weeds are rich in micro-nutrients, like, Fe, Cu and Zn. The release of the micro-nutrients, on the decomposition of soil organic matter, might have caused additional benefits to the crop.

TABLE IV(*a*)

Effect of different weeds added as a source of organic matter on dry matter production and nutrient uptake under submerged conditions. (paddy crop)

Treatments	Dry-matter yield (gm./pot)			Nutrient Uptake (mg/Pot)								
				Nitrogen (N)			(Phosphorus P_2O_5)			Potassium (K_2O)		
	Grain	Straw	Total	Grain	Straw	Total	Grain	Straw	Total	Grain	Straw	Total
	(Mean of three replications)											
C. Control	7·62	13·88	21·50	89·92	55·52	145·44	48·77	29·15	77·92	23·62	158·23	181·85
1. Soil + *T. monogyna*	13·74	27·16	40·90	159·38	105·92	265·30	85·19	54·32	139·51	41·42	304·19	345·41
2. ,, + *L. camara*	12·12	23·25	35·37	141·80	88·35	230·15	76·36	48·82	125·18	37·57	265·05	302·62
3. ,, + *H. eichwaldii*	16·78	31·85	48·63	192·97	124·21	317·18	104·04	63·70	167·74	50·34	356·72	407·06
4. ,, + *C. sparsiflorus*	19·74	39·52	59·26	225·04	146·22	371·26	124·36	82·99	207·35	61·19	450·53	511·72
5. ,, + *C. sativa*	21·15	43·94	65·09	236·88	166·97	403·85	131·13	87·88	219·01	63·45	492·13	555·58
6. ,, + *X. strumarium*	17·41	35·63	53·04	205·44	142·52	347·96	107·94	74·82	182·76	53·97	406·18	460·15
7. ,, + *C. oxyacantha*	11·86	22·09	33·95	139·95	86·15	226·10	74·71	44·18	118·89	35·58	247·41	282·99
S. Ems	±1·03	±2·31	±3·23	±3·63	±4·80	±9·14	±2·58	±1·78	±4·44	±1·50	±11·11	±11·77
C. D. at 5%	2·95	6·62	9·26	10·55	13·76	26·20	7·39	5·10	12·73	4·30	31·82	33·54
C. D. at 1%	3·96	8·88	12·42	14·16	18·48	35·14	9·92	6·86	17·07	5·78	42·69	45·38

TABLE IV(*b*)

Effect of different weeds added as a source of organic matter on dry matter production and nutrient uptake under well-drained conditions. (wheat crop)

Treatments	Dry-matter yield (gm/pot)			Nutrient Uptake (mgm/pot)								
				Nitrogen (N)			Phosphorus (P_2O_5)			Potassium (K_2O)		
	Grain	Straw	Total	Grain	Straw	Total	Grain	Straw	Total	Grain	Straw	Total
	(Means of three replications)											
C. Control	3·20	5·25	8·45	58·88	22·05	80·93	26·56	9·92	35·48	11·52	48·82	60·34
1. Soil + *T. monogyna*	5·12	9·93	14·05	91·65	35·72	127·37	41·47	14·29	55·76	17·92	82·16	100·08
2. ,, + *L. camara*	1·74	3·11	4·85	31·32	12·13	43·45	14·27	5·29	19 56	6·26	28·92	35·18
3. ,, + *H. eichwaldii*	5·45	8·10	13·55	96·46	32·40	128·86	44·14	12·96	57·10	19·07	74·52	93·59
4. ,, + *C. sparsiflorus*	6·26	10·54	16·80	107·67	40·05	147·72	51·33	17·92	69·25	22·54	98·02	120·56
5. ,, + *C. sativa*	6·75	10·35	17·10	114·75	40·36	155·11	54·00	16·56	70·56	23·62	95·22	118·84
6. ,, + *X. strumarium*	5·10	7·85	12·95	93·84	32·97	126·81	41·31	13·34	54·65	18·36	73·00	91·36
7. ,, + *C. oxyacantha*	1·35	2·55	3·90	24·43	10·46	34·89	11·077	4·08	15·15	4·72	23·46	28·18
S. Ems	±0·22	±0·31	±0·46	±0·41	±1·34	±4·97	±2·05	±0·69	±2·45	±1·19	±4·43	±5·49
C. D. at 5%	0·63	0·89	1·32	11·75	3·84	14·25	5·87	1·98	7·02	3·41	13·70	15·74
C. D. at 1%	0·85	1·20	1·77	15·82	5·15	19·11	7·88	2·65	9·46	4·58	17·04	21·11

EFFECT OF DIFFERENT WEEDS AS A SOURCE OF ORGANIC MATTER ON DRY-MATTER PRODUCTION (GRAIN, STRAW AND TOTAL YIELD)

FIG. 1

ADDED ONE MONTH BEFORE SOWING WHEAT SEEDS

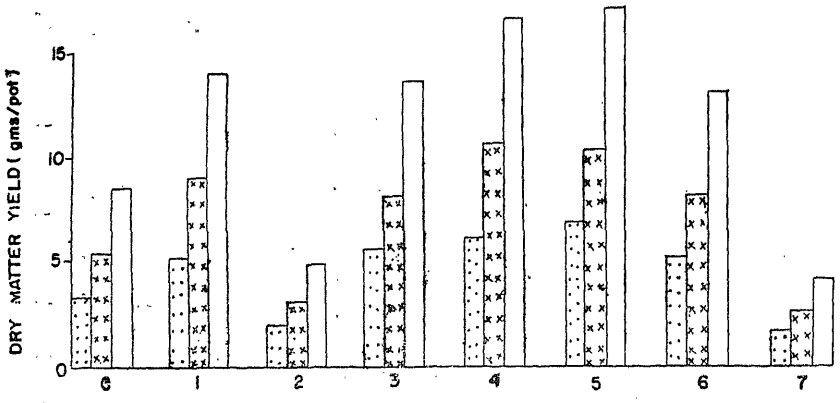
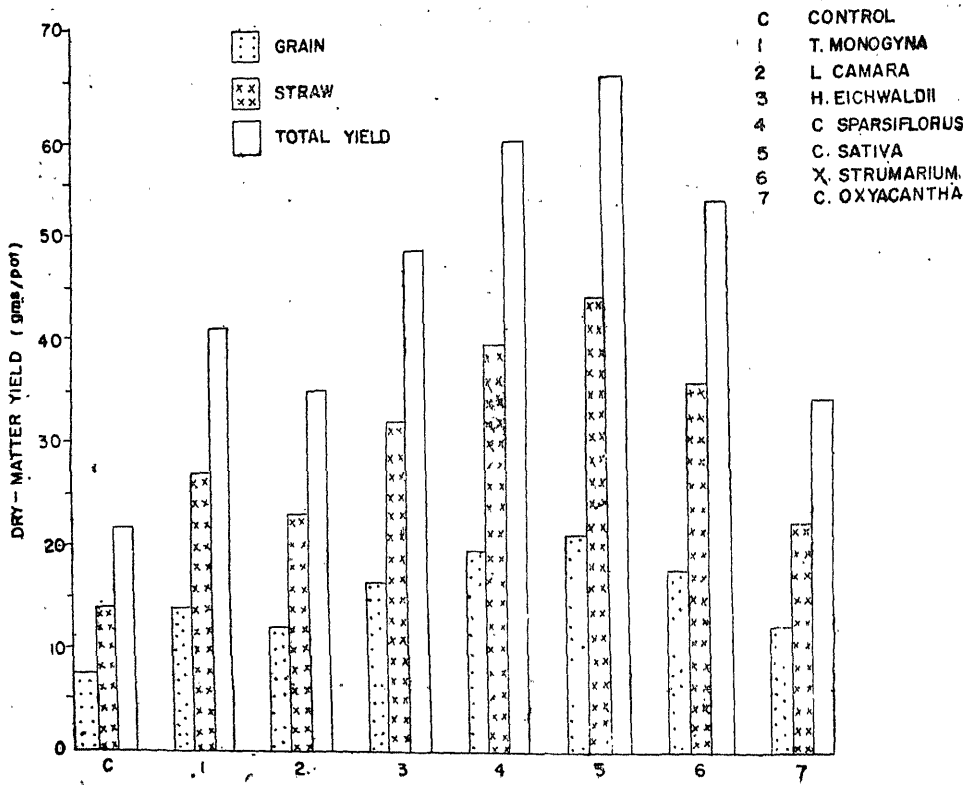


FIG. 2

ADDED ONE MONTH BEFORE TRANSPLANTING PADDY SEEDLINGS



The dry matter yield obtained with wheat and paddy crops is represented in Figs. 1 and 2. It is observed that on the application of the same weed under submerged conditions, more yield is obtained as compared to well drained conditions. This is in close agreement with the results of the incubation experiments in which more of available N, P, K was found under submerged conditions than in well drained soils.

It is evident from the present study, that weeds which are plentifully available, in all the seasons of the year, under diverse soil and climatic conditions promise a vast scope for the replenishment of soil humus, thereby soil fertility, and increased crop production, especially under submerged conditions.

Summary

Seven commonly available weeds, namely, *Trinthum portulacastrum*, *Lantana camara*, *Heliotropium eichwaldii*, *Croton bonplandianum*, *Cannabis sativa*, *Xanthium strumarium* and *Carthamus oxyacantha* were collected at flowering stage and chemically analysed for their inorganic, organic and trace element composition. The analytical data showed that weeds contained total nitrogen upto 3·7%, phosphorus as P_2O_5 1·8% and potassium as K_2O 7·5%. Besides, these primary nutrients weeds were also found rich in Ca and micro-nutrients, like Fe, Zn and Cu.

Green house experiments conducted with paddy and wheat on the alluvial soil revealed that the addition of weeds resulted in significant increase on dry matter production and nutrient uptake in respect of N, P and K. Data indicated that under submerged conditions all weeds gave significantly higher yields. Under well-drained conditions, *L. camara* and *C. oxyacantha* gave lower yields, even when compared to control, The lowering of yield, observed with these two weeds may be related to their high C : N and lignin content. This effect of environments on the mineralisation of soil nitrogen indicates that under submerged conditions, there is less danger of nitrogen immobilisation.

Acknowledgements

Thanks are due to Dr. N. P. Datta, Head of the Division of Soil Science and Agricultural Chemistry for providing necessary laboratory facilities and to C. S. I. R. for providing a fellowship to one of the authors during the course of the study.

References

1. Annonymous. *IRC working party on fertilizers, Bangkok IRC/FP/53/39*, 1953.
2. Basu, J. K. and Sirur, S. S. *Ind. Jour. Agri. Sci.* **13** : 66-86, 1943.
3. Bear, F. E. Soils and Fertilizers. *John Wiley and Sons, Inc., New York*, 1953.
4. Bremner, J. M. *J. Soil Sci.*, **5** : 214-232, 1954.
5. Ibid. *Soils and Fertilizers*, **19** : 115-123, 1956.
6. Broadbent, F. E. *Advan. Agron.*, **5** : 115-123, 1953.
7. Ibid. *Soil Sci.*, **79** : 107-114, 1955.
8. Chapman, H. D. and Pratt, P. F. *Method of analysis for soils, plants and waters, University of California*, 1965.
9. Deuel, H., Dubach, P., Mehta, N. C. and Bach, R. *Schweiz. Z. Hydrol*, **22** : 111-121, 1960.
10. Dhar, N. R. *Presi. Address to the 48th Indian Sci. Congr., Roorkee*, 11, 1961.

11. Dhar, N. R. and Singh, G. *Proc. Nat. Acad. Sci., India,* **34A** (3) : 1964.
12. Dickman, S. R. and Bray, R. H. *Indus. Engg. Chem. Anal. Ed.,* **2** : 665 68, 1940.
13. Dubach, P. and Metha, N. C. *Soils and Fertilizers,* **26** : 293-300, 1963.
14. Dubach, P., Mehta, N. C., Jakab, T., Martin, F. and Roulet, N. *Geochim. Cosmochim. Acta,* **28** : 1567-78, 1964.
15. Ferguson, W. H. *Canad. J. Soil Sci.,* **37** : 145-46, 1956.
16. Flaig, W. *Suomen Kemistilehti,* A**33** : 229-251, 1960.
17. Fred, E. B. and Waksman, S. A. Lab. Manual Gen. Microbio. *Mc Graw Hill Book Co., New York,* 1928.
18. Fuller, W. H. Soil organic matter. *Bull. A* 40. *Co-operative Extension service and Agril. Exp. Sta., Univ. Arizona,* 17, 1965.
19. Hanway, J. and Heidal, H. Soil aanlysis methods used in Iowa State College. *Soil Testing Lab., Iowa, Agric.,* **57** : 31, 1962.
20. Jackson, M. L. Soil Chemical Analysis. *Prentice-Hall, Inco. Englewood, Cliffs, N. J.,* 1958.
21. Kononova, M. M. Soil Organic Matter. *(Transl. by T. Z. Nowakowski and G. A. Greenwood) Pergamon Press, Oxford,* 1961.
22. Miller, C. E. and Turk, L. M. Fundamentals of Soil Science. *Chapman and Hall, Ld. London,* 1951.
23. Mortensen, J. L. *Soil Sci. Soc. Am. Proc.,* **27,** 179-186, 1963.
24. Nagar, B. R. *Ann. Rept. Sch. Humification Organic matter. Agra Coll., Agra,* 1956.
25. Nagar, B. R. and Dutta, N. P. *Jour. Sci. Ind. Res.,* **26** : 1-4, 1967.
26. Olsen, S. R. *et al. U. S. D. A. Cir.* 939, 1954.
27. Peevy, W. J. and Norman, A. G. *Soil Sci.,* **65** : 209-226, 1948.
28. Pieters, A. J. Green-manuring. *John Wiley and Sons, New York,* 1927.
29. Pink, L. A., Allison, F. E. add Gaddy, V. L. *J. Amer. Soc. Agron.,* **40** : 237-248, 1948.
30. Piper, C. S. Soil and Plant Analysis. *Univ. of Adelaide, Australia,* 1950.
31. Prasad, M. and Dange, G. V. *Ind. Forest Leaflet,* **95** : 1-27, 1947.
32. Scheffer, F. and Ulrich, B. Humus and Humus dlingung. *Ferdinand Enke, Stuttgart,* **1** : 1960.
33. Singh, B. N. and Singh, L. B. *Soil Sci.* **47** : 227-30, 1939.
34. Spaulding, M. F. and Eisenmenger, W. S. *Soil Sci.,* **45** : 427-45, 1938.
35. Sprague, H. B. *New Jersey Agri. Expet. St. Bull.,* **609** : 19, 1936.
36. Subbiah, B. V. and Asija, G. L. *Curr. Sci.,* **25** : 259-60, 1956.
37. Vimal, O. P. Effect of bagasse, ammonium sulphate and superphosphate on carbon, nitrogen and phosphorus tranformations in an alluvial soil. *M.Sc. Thesis, IARI,* 1964.
38. Whitehead, D. C. *Soils and Fertilizers,* **26** : 217-23, 1963.
39. Winsor, G. W. and Pollard, A. G. *J. Sci. Food Agri.,* **7** : 134-41, 1956.
40. Zenobius, S. *Compost Sci.,* **3**(1) : 36-39 ; 2, 27-32, 1962.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968.

Cultivation of Some Selected Vegetables/Crops in the Allahabad Climate and Soil

By

R. B. BOSE *and* G. PANIGRAHI

Central Circle, Botanical Survey of India, Allahabad

Professor Hutchinson (1966) ascribes the present food crisis in India causing famine risks, to the uncertainty in rainfall and to the low fertility of our lands beyond the village borders. He is, however, highly optimistic that the improvement of the fertility of our land is possible within 20 years from hence, if only we learn to change our age old-habits and customs necessary to establish the systematic conservation and distribution of the organic manures locally abundant in the area (as distinct from artificial fertilisers) and get over the social intertia which stands in the way of radical land refom. Considering the abundance of organic manures available and the high cost of artificial manures, he advocates more of local incentives than knowledge to make India self-sufficient in food. According to him, only rich can squander the organic manures. Thus, Hutchinson corroborates Dhar's view in these respects, Prof. Dhar being one of the most outstanding and consistent advocates of the efficacy of organic manures over the artificial manures in the conditions prevailing in our country.

There is, however, another school of thought who redicule the possiblity of increasing food production by "using the same old plant and animal materials on the same old soil in the same old ways". They advocate the initiation of a new strategy of agricultural development by the use of high-yielding varieties of wheat, rice, maize, Jowar and bajra, developed in recent years and by the use of artificial fertilisers. They maintain, "If only the requisite inputs can be produced quickly on a scale that is needed to satisfy the demands of the cultivators and if the knowledge of the new technology can be spread in the villages quickly, we have every reason to hope that our agriculture would soon reach a buoyancy essential for raising the standard of living of our people".

A critical study of these views on the question of bringing spectacular rise in food production in India brings out the following salient points :

1. While there is no unanimity regarding the practicability of large scale application of artificial fertilisers or "inputs" by the poverty-stricken agriculturists of India, opinions in favour of the use of organic waste/manure, available locally in abundance, are vigorously growing.

2. Improved genetically superior seeds/propagules must replace the age-old seeds/propagules raised from the parent stock on year to year basis, since the latter have attained near-homozygosity in their genetic contents and lack not only the hybrid vigour but the capacity to withstand the onslaughts of plant diseases and insect pests.

3. Large-scale multiplication of minor irrigation projects, *viz.* digging of deep water wells, and tube-wells for each farm will benefit the farmer, specially in the non-hilly areas, since this would ensure irrigation of his crop in times of need arising out of the vagaries of monsoon and rainfall.

TABLE I

Sl. No.	Vegetables	Date of sowing	Date of germination	Date of transplantation	Direct sowing followed by thinning	Area (sq. metre)	Spacing (cms)	Cultural methods and practices	Period of fruiting harvesting
1	Brinjal	August	–	27-9-65	–	112	60×45	The field for planting brinjals has to be thoroughly prepared as the plants will remain in the field for a long time. 1½ quintals of F. Y. M. was mixed with the soil of the plot 2–3 days before transplantation. When the seedlings were two months old, a light howing had been made followed by top dressing with Neem Cake (10 kg.) and Ammonium Sulphate (2 kg.)	December to August
2	Tomato	do	–	27-9-65	–	80	60×45	1 quintal F. Y. M. Top-dressing with Neem Cake (3-5 kg.) + Ammonium Sulphate (1½ kg.)	January to March
3	Chille	–	–	28-9-65 and 29-9-65	–	104	45×45	do (No neem cakes added)	January to April
4	Carrot	29-9-65	7-10-65	–	Thinning done one month after (from the date of sowing)	32	5–8	Soil of the plot was made loose with spades. 30 kgs. of F. Y. M. was mixed in the plot 4 days before transplantation. 1½ month old seedlings were top-dressed with 1·5 kg. of Ammonium Sulphate.	December to January
5	Turnip	29-9-65	3-10-65	–	do	16	do	do (15 seers of F. Y. M. was mixed with the soil)	do
6	Radish	29-9-65	2-10-65	–	do	28	8–10	28 seers of F. Y. M. was added in soil 4-5 days before transplantation. The seedlings were raised in ridges to facilitate irrigation. Top-dressed with Amm- Sulphate as in '4' & '5' above.	do
7	Spinach	29-9-65	4-10-65	–	do	8	5-6	8 seers of F. Y. M. was mixed with soil 4–5 days before transplanation of seedlings. No top-dressing made.	do

8	Onion	30-9-65	5-10-65	31-12-65	–	400	10–12	The plots for transplanting Onion seedlings were prepared carefully and the soils were made loose. 1 quintal of F. Y. M. was mixed with the soil 7 days before transplantation. $2\frac{1}{2}$ month old plants were top-dressed with Ammonium sulphate (15 kg.)	March to April
9	Lettuce	30-9-65	7-10-65	8-11-65	–	8	20	$1\frac{1}{2}$ months old seedlings were transplanted. No manures and fertilizers added.	January
10	Cauliflower	–	–	29-10-65	–	12	40–45	12 kgs. of F. Y. M. was mixed with the soil 5-6 days before transplantation of seedlings.	December to January
11	Cabbage	1-11-65	5-11-65	6-12-65	–	380	40–45	About 1 quintal of F. Y. M. was mixed in the soil 7 days before transplantation. One month old seedlings were transplanted. 6 weeks old seedlings were top-dressed with 15 kg. of Ammonium sulphate.	January to February
12	Knol-Khol	6-12-65	9-12-65	31-12-65	–	84	20–30	No manures were added. Seedlings were top-dressed with Ammonium sulphate. (3 kg.)	do
13	Potato	4-12-65	20-12-65	–	Planted	450	30	The plot was thoroughly ploughed. Clods were broken, weeds and stone chips were also removed. $2\frac{1}{2}$ quintals of F. Y. M. and 20 kg. of Ammonium sulphate were thoroughly mixed with the soil 4–5 days before sowing.	March
14	Snake-Cucumber (Kakri)	7-2-66	14-2-66	2-3-66	–	450	–	50 holes (3/4 × 3/4 m.) were prepared and in each hole 2 kg. of F. Y. M., 3 kg. of leaf mould and 10 gms. of Ammonium sulphate, were mixed thoroughly 7 days before the transplantation of seedlings.	March to May

Sl. No.	Vegetables	Date of sowing	Date of germination	Date of transplantation	Direct sowing followed by thinning	Area (sq. metre)	Spacing (cms.)	Cultural methods and practices	Period of fruiting harvesting
15	Bitter-gourd (Karela)	7-2-66	14-2-66	3-3-66	–	450	–	50 holes (3/4×3/4 m.) were prepared and in each hole 2 kg. of F. Y. M., 3 kg. of leaf mould and 10 gms. of Ammonium sulphate were mixed thoroughly 7 days before the transplantation of seedlings.	March to August
16	Ash-gourd (Kumrah)	7-2-66	14-2-66	3-3-66	–	450	–	do	March to May
17	Bottle-gourd (Louki)	7-2-66	14-2-66	4-3-66	–	450	–	do	March to August
18	Lady's Finger (Bhindi)	7-7-66	13-7-66	–	Sown in lines	500	45–50	Seeds are soaked for few hours before sowing. 3 quintals of leaf-mould was thoroughly mixed with the soil, 8–10 days before transplantation of seedlings.	August to October
19	Bottle-gourd (Louki)	7-7-66	14-7-66	2-8-66	–	450	–	50 holes (3/4×3/4 m.) were prepared and in each hole 2 kg. of F. Y. M., 3 kg. of leaf-mould and 10 gms. of Ammonium sulphate were mixed thoroughly 7 days before the transplanatation of seedlings.	November to December
20	Aroids (Arvi)	15-7-66	1-8-66	–	Planted in lines	264	45-50	Rhizomes are planted in lines. Irrigation made immediately after planting; 1 quintal of leaf-mould, ½ quintal of F. Y. M. and 2 kg. of Ammonium sulphate were thoroughly mixed with soil 3–4 days before transplantation.	November

21	Maize "Ganga Macca 101"	22-7-66	28-7-66	–	Sown in lines	500	30×25	The field was carefully prepared by making the soil loose and by removing stone chips, clods etc. ; 3½ quintals of leaf-mould and 3 quintals of F. Y. M. were thoroughly mixed with the soil 4–5 days before sowing. Seeds were sown in lines.	September-October
22	Cowpea (Lobia)	23-7-66	27-7-66	–	do	500	75×150	Seeds are sown in lines. 2½ quintals of leaf-moulds was applied 4 days before sowing of seeds.	do
3	Sweet Potato	8-8-66	16-8-66	–	do	276	60×20	Propagated through cuttings. They are raised in ridges. 2½ quintal leaf-mould was mixed with the soil about 10 days before sowing,	December
24	Brinjal	22-6-66	27-6-66	4-8-66	–	280	75×60	2½ quintals of leaf-mould were mixed with soil about two weeks before the transplantation of seedlings. No other manures/fertilisers were added.	October
25	Lettuce	16-9-66	22-9-66	14-10-66	–	18	30	1½ months old seedlings were transplanted. 10 kg. of F. Y. M. added few days before transplantation of seedlings.	December-February
26	Radish (White)	20-10-66	25-10-66	–	Sown in lines	27	8-10	28 kg. of F. Y. M. was added in soil 4–5 days before transplantation. The seedlings were raised in ridges to facilitate irrigation. Top-dressed with 5 kg. of F. Y. M. and mixed with soil 5–6 days before sowing.	December-January
27	Radish (red)	20-10-66	25-10-66	–	do	9	do	do 12 kg. of F. Y. M. was added.	do
28	Spinach (Palang)	27-10-66	2-11-66	–	do	36	5–6	50 kg. of F. Y. M. was mixed with soil 4–5 days before transplantation of seedlings. No topdressing made. 50 kg. of F. Y. M. was mixed with the soil 7 days before sowing.	do
29	Turnip	20-10-66	26-10-66	–	do	27	10-12	do (40 kg. F. Y. M.)	do
30	Beet	20-10-66	30-10-66	–	do	9	15-20	do (15 kg. ,,)	February
31	Carrot	27-10-66	6-11-66	–	do	36	10-12	do (40 kg. ,,)	do

TABLE II

Sl. No.	Vegetables	Month of sowing	Period from sowing to harvest (in months)	Yield (kg.)	Area (sq. metre)	Quantity of fertilisers/manures applied in kg.			
						F. Y. M.	Am. sulphate	Leaf-mould	Neem-cake
1	Onion	October	6–7	185	400	100	15	–	–
2(*a*)	Brinjal	August	11	86	112	150	2	–	10
2(*b*)	Brinjal	June	11	290	276	–	–	250	–
3	Carrot	October	3	48	32	30	1·5	–	–
4	Potato	December	4	250 kg. approx.	450	250	20	–	–
5	Bottle-gourd (Lauki)	February	6	269 nos.	480	30	5	–	–
6	Snake-cucumber (Kakri)	do	4	500 nos.	450	30	5	–	–
7	Ash-gourd (Kumrah)	do	4	35 nos.	450	25	5	–	–
8	Lady's Finger (Bhindi)	July	4	55	500	–	–	300	–
9	Sweet Potato	August	5	120	276	–	–	250	–
10	Radish (Red)	October	3	33	9	12	–	–	–
11	Spinach (Palang)	do	3	47	36	50	–	–	–
12	Turnip	do	3½	130	27	40	–	–	–

Botanical names of vegetables/crops mentioned in table I

1.	Brinjal	.. *Solanum melongena* Linn.
2.	Tomato	.. *Lycopersicon lycopersicum* (Linn.) Santapau
3.	Chille	.. *Capsicum annum* Lim. var. *acuminatum* Fingh.
4.	Carrot	.. *Daucus carota* Linn. var. *sativa* DC.
5.	Turnip	.. *Brassica rapa* Linn.
6.	Radish	.. *Raphanus sativus* Linn.
7.	Spinach	.. *Beta vulgaris* Linn. var. *benghalensis* Roxb.
8.	Onion	.. *Allium cepa* Linn.
9.	Lettuce	.. *Lactuca sativa* Linn.
10.	Cauliflower	.. *Brassica oleracea* Linn. var. *botrytis* Linn.—Snow ball.
11.	Cabbage	.. *B. oleracea* Linn. var. *capitata* Linn.
12.	Knol Khol	.. *B. oleracea* Linn. var. *gongyloides* Linn.
13.	Potato	.. *Solanum tuberosum* Linn.
14.	Snake-Cucumber	.. *Cucumis melo* Linn.
15.	Bitter-gourd	.. *Momordica charantia* Linn.
16.	Ash-gourd	.. *Benincasa hispida* (Thunb.) Cogn.
17.	Bottle-gourd	.. *Lagenaria siceraria* (Mol.) Standl.
18.	Lady's finger	.. *Hibiscus esculentus* Linn.
19.	Aroid	.. *Colocasia esculenta* (Linn.) Schott.
20.	Maize	.. *Zea mays* Linn.
21.	Cowpea	.. *Vigna cylindrica* Skeels
22.	Sweet Potato	.. *Ipomoea batatas* Linn.
23.	Beet	.. *Beta vulgaris* Linn.

Bearing these points in mind and to give practical content to the policy of "Grow more Food" campaign initiated by the Government of India during the crucial Indo-Pakistan war, we, in the Central Circle of the Botanical Survey of India, set apart a plot of about 0·57 acres of land (2880 sq. metres) at Allahabad, for growing a few selected vegetables in the alluvial loam of the gangetic valley.

We have cultivated as many as 23 vegetables during the last 16 months in small plots, beds etc. While the yield of some of the vegetables was fair or even poor, the vegetables like Lady's finger, Brinjal, Bottle-gourd, Cucumber, Ash-gourd, Sweet Potato, Onion, Carrot, Turnip, Radish, Palak etc. were grown with good yield. The names of the vegetables/crops grown, the date of sowing, germination, transplantation, the area over which the crop is grown and the spacing between individual plants, cultural methods and practices and the period of fruiting are presented for all the 23 vegetables in Table I. Table II provides the available data on the 12 selected vegetables which were successfully cultivated in the Experimental conditions.

A critical study of these data furnished in Table I and II suggests the following tentative findings :

Failure to select seeds/propagules in the beginning, may result not only in financial loss but in psychological set-back to the farmer ; the purchase of such materials (*viz.* Cauliflower and Cabbage in our case) from Govt. farm/nursery is no guarantee of the genetically superiority of the material concerned.

The vegetables cultivated by us are definitely seasonal in nature ; the month of sowing of seeds/propagules and period of transplantation of seedlings, profoundly affect the growth, development and yield. Cultivation of the same crop raised from seeds from same stock in the wrong season, may affect adversely the yield, *viz.* Brinjal and Lauki in the above table.

With very poor irrigational facilities, either due to failure of rain or due to non-availability of adequate water supply from the well, Onion is a more prospective cash-crop than Potato.

Even the high yielding strain of Maize (Gange Macca-101) which is recommended for the Gangetic plain, cannot also guarantee good yield if adequate irrigation and requisite application of manures are not provided with. In 500 sq. meters of land we added 3½ quintals of leaf-mould and 3 quintals of F. Y. M. for cultivation of this crop but it yielded only about 200 cobs, in which the fruit setting, again was not satisfactory.

Application of about 2½ quintals of compost or leaf-mould (derived from the rotting of the weeds and vegetable matter discarded from the garden after harvesting of other ornamental plants or crops) to the plot of about 300 sq. m., yielded about 275 kg. of brinjal fruits. In the previous season, application of 1½ quintals of Farm yard manure (cowdung mainly) and 2 kg. of Ammonium Sulphate and top-dressing of Neem-cake to a plot of 112 sq. m., yielded only 86 kg. of brinjals. This yield compares favourably with average yield of 8000–10000 kgs. of brinjals per acre to which 10-15 tons of F. Y. M. was supplemented with fertilisers to supply 45 kgs. nitrogen and 22 kgs. each of Phosphate and Potash (*cf* F. B. No. 31, 1965). Leaf-mould as a source of organic nutrition to the crop is witnessed again from the good yield of Sweet Potato, Lady's finger, Turnip and Carrot to which neither F. Y. M. or Ammonium sulphate was added. Tomato, as a cash-crop, may often be deceptive on account of its high susceptiblity to virus infection.

Bottle-gourd (Louki) and Cucumber (Kakri) are by far the most suitable vegetables for Allahabad climate from February onwards and are presumably

Nature's gift to withstand the rigours of the 'loo' wind. The plants thrive well even under extreme drought conditions, if the seedlings were transplanted in holes 3/4×3/4 m. depressions, each filled with a mixture of 2 kg. of F. Y. M. + 3 kg. of leaf-mould + 20 gms. of Ammonium Sulphate, about a week before.

In case of root-crops, such as radish, beet root, turinp etc., irrigation from the well is totally discontinued a week before harvest to retain the taste and colour of the produce (Farm News No. 39/(6).

To further corroborate the above tentative findings based on only 16 months of experimental study a more comprehensive programme is being laid out for the subsequent year.

Summary

The question of bringing about spectacular rise in food production in India, engages serious attention of many, both in our country and abroad. While there is no unanimity regarding the practicability of large scale application of artificial manures by the poverty-stricken agriculturists, Dhar in India and Hutchinson in England, amongst others, are great votaries of the efficacy of organic manures for the improvement of the fertility of our lands. The extensive use of organic manures together with the genetically improved superior seeds/propagules, aid d by minor irrigation projects, specially in non-hilly areas, are considered to hold the key to the solution of the ever-increasing food crisis in India.

Bearing these points in mind, some 22 vegetables and the maize crop were raised in small plots within the total area of about 2880 sq. metres during 1965 and 1966. The names of veg tables grown, the date of sowing, germination, transplantation, the area over which the crop was grown and the spacing between individual plants, notes on cultural methods and practices, and the period of fruiting and the total yield of each, are presented in tabular forms.

Certain tentative findings regarding, (*a*) the selection and purchase of good seeds/propagules even from Government Nurseries, (*b*) the seasonal nature of vegetables, some of which are suitable for cultivation only in specific months of the year, (*c*) procurement of good yield from the application of leaf-mould and F. Y. M., not supplemented by artificial manures, and (*d*) regarding the absolute necessity for ensuring adequate irrigation to the crops, have been discussed in the paper.

To further corroborate the above findings based on only 2 years of study, a more comprehensive experimental programme is being laid out for the subsequent years.

Acknowledgements

Grateful thanks are due to Father H. Santapau, S. J., Padma Shree, Director, Botanical Survey of India, Calcutta for kind interest and encouragement.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968.

Determining Mn availability in certain soil groups of Uttar Pradesh

By

S. G. MISRA *and* P. C. MISHRA

Agricultural Chemistry Section, Department of Chemistry, Allahabad University, Allahabad.

Though manganese has been recognized as an essential plant nutrient since long but it has been suggested that no correlation exists between the total manganese of the soil and the manganese available to plants. Consequently a number of workers have tried to find out the factors affecting the availability of manganese in soils. Christensen, Toth and Bear (1950) have found that manganese status in soils is influenced by soil moisture, organic matter and pH, whilst Heintze (1957) has shown that some of the divalent form of manganese is present as a complex of the organic matter which can not be extracted by ammonium acetate or hydroquinone. Boischot (1950) has shown that the availability of manganese is greatly influenced by the amount of $CaCO_3$ present in soils However, data regarding the transformation of added Mn^{++} to different soils are not available.

The present work was therefore undertaken with a view to study the fate of applied manganese (Mn^{++}) to three different groups of soils, namely the black, the red and the alkali soils from Uttar Pradesh under different sets of conditions.

Experimental Procedure

Soil samples used in the present study were collected from three different districts of Uttar Pradesh. The alkali soil sample was collected from a large alkali affected patch of soils near Soraon (Allahabad district). The black soil sample was collected from Ballia and the red soil from Khantara, a village situated in the interior of hilly region of Mirzapur district.

Soil samples were air dried, powdered and sieved by a standard sieve and then oven dried. 10 gms of the samples were used for the preparation of HCl-extract. The amount of total calcium was determined by usual method by taking a suitable aliquot of HCl extract. Carbon was determined by Walkley Black's rapid titration method. Native total manganese in the soil was determined by Na_2CO_3 fusion method (Jackson, 1962). The fused mass was treated with sufficient water to digest the fused cake and then 30 ml of concentrated HCl was added. Silica was separated by dehydrating it and manganese in the filtrate was determined colorimetrically after developing the colour with potassium periodate. Exchangeable manganese was determined colorimetrically in the leachates obtained after leaching the soils with neutral normal ammonium acetate. In order to determine the reducible manganese in soil, the soil obtained after ammonium acetate treatment was further leached with 0·2% hydroquinone in neutral normal ammonium acetate. The Mn in the leachate was determined colorimetrically as in the case of total Mn.

Soluble manganese was added in the form of $MnSO_4$, solution (1 : 10 soil solution ratio) and the contents were shaken in a flask and kept over night. Next day the soil was seperated from the filtrate, washed with distilled water (in order

to remove any adhering manganese on the surface) and the manganese was determined colorimetrically in whole of the leachate. This treated soil after being completely washed with distilled water was then used for determining exchangeable and reducible forms of soil manganese. In each case a blank was run side by side and the amounts of Mn determined in various forms in these blanks was subtracted from the amounts of various forms of manganese in the Mn^{++} treated soils.

TABLE 1

Chemical characteristics of the soils used

Soils	%organic carbon	%total carbonates as $CaCO_3$	%soluble carbonates	Cation exchange capacity. m.e/100g.	pH	Manganese in ppm		
						Exchangeable	Reducible	Total
Black	0·52	1·75	Nil	39·5	8·0	225	226	900
Red	0·76	0·875	Nil	24·0	6·4	40	150	250
Alkali	0·51	16·0	0·33	6·6	9·7	6	10	265

Effect of pH: pH of the soil with Mn^{++} solution was varied from 6·0 to 4·0 by adding dilute H_2SO_4.

Effect of Carbonate: For this purpose hydrogen soil prepared by treating the original soil with N/10 HCl has been used. The $CaCO_3$ has been varied from 1% to 8%. Retention studies in the absence of $CaCO_3$ have also been carried out.

Effect of Organic matter: In this study, addition and destruction of organic matter have been tried. Organic matter has been destroyed by hydrogen peroxide treatment varying from 1 ml to 20 ml. In order to find out the effect of adding organic matter to soils, the total organic matter of the soils was destroyed and then humus was added varying from 1% to 4%.

The following abbreviations have been used to denote different forms of Mn. The amounts of Mn have been expressed in ppm.

R = Mn^{++} retained

E = Exchangeable manganese

r = Reducible manganese

A = Active manganese (E+r)

F = Fixed form.

Results and Discussion

From the results given in table 2 it is evident that the black soil, the red soil and the alkali soil retained varying amounts of added Mn^{++}. The three soils vary with respect to their contents of organic matter, calcium carbonate and pH values. It is well established that organic matter, calcium carbonate and pH of the soils affect the retention of applied manganese. Alkali soil retained almost all the manganese applied whereas the red soil retains the least whilst the black soil occupies an intermediate position. The cent percent retention by alkali soil may be due to the precipitation of manganese in alkali soils.

Amount of exchangeable and reducible manganese also increase as the amount of manganese applied to soil is increased. Reducible and fixed form of manganese is highest in the case of the alkali soil whilst is lowest in the case of the red soil.

TABLE 2

Retention of manganese by the soils

Concentration of manganese (ppm)	Mangenese retained (ppm) (R)	Forms in which Mn^{++} is retained (ppm) E	r	A	F	A/R
Black soil						
105	103	30	12	42	61	0·40
525	509	303	100	403	106	0·79
1050	976	654	186	840	136	0·86
Red soil						
105	98	72	16	88	10	0·90
525	405	284	72	356	49	0·88
1050	668	454	132	586	78	0·88
Alkali soil						
105	105	17	36	53	52	0·50
525	519	203	174	377	142	0·72
1050	1039	386	354	740	299	0·71

TABLE 3

Effect of equilibrium pH on retention of manganese by the soils

Concentration of the Mn added—1050 ppm

Equilibrium pH	Mn. retained in ppm (R)	Forms in which Mn^{++} is retained (ppm) Exchangeable	Reducible (r)	E+r=A	R–A=F	A/R
Black soil						
6·0	894	568	144	712	182	0·79
5·5	876	552	144	696	180	0·79
5·0	848	544	136	680	168	0·80
4·5	828	524	137	661	163	0·80
4·0	786	518	110	628	158	0·80
Red soil						
6·0	585	376	62	438	147	0·748
5·5	580	372	62	434	146	0·748
5·0	544	354	56	410	132	0·750
4·5	506	338	50	388	118	0·760
4·0	470	313	39	357	113	0·770
Alkali soil						
6·0	322	64	50	114	208	0·350
5·5	264	102	48	150	114	0·600
5·0	248	110	48	150	90	0·603
4·5	234	110	48	158	76	0·670
4·0	202	120	36	156	46	0·770

Effect of pH on the retention of Manganese : From the results given in table 3 it is observed that the lower the equilibrium pH, the lower is the retention. It is quite marked in the case of alkali soil where the retention at pH 4·0 is only 23% of the added Mn whereas in the case of original soil it is 98·0%. However reducible form of manganese does not show any marked change as the pH is lowered. On the contrary black and red soils show gradual decrease in exchangeable and reducible forms of manganese as the pH is lowered. Alkali soil shows an increase in the exchangeable manganese as the pH is lowered.

Effect of Calcium carbonate : From the data recorded in table 4 it is observed that $CaCO_3$ is no doubt responsible for the retention and fixation of manganese. The effect of calcium carbonate is more marked towards the increased retention in the case of the red and the alkali soils. Exchangeable manganese shows a gradual decrease with increase in the calcium carbonate added whilst the reducible form of manganese increases with increase in the amount of manganese added to the soil. Amount of manganese fixed (not extracted by the extractants used) also increases with increase in the added $CaCO_3$ content.

TABLE 4

Effect of Carbonate on the retention of Manganese

Concentration of Mn added = 1100 ppm

% $CaCO_3$ added to H-soil	R.	Forms in which Mn is retained (ppm) E	r	A	F	A/R
Black Soil						
Nil	944	630	70	700	244	0·740
1	941	630	73	703	238	0·747
2	938	614	77	691	247	0·736
4	958	540	144	684	274	0·710
6	972	504	182	686	286	0·700
8	992	460	232	692	300	0·697
Red Soil						
Nil	380	319	37	356	24	0·930
1	650	450	41	491	159	0·755
2	686	436	52	488	198	0·710
4	705	423	62	485	220	0·688
6	745	388	115	503	237	0·660
8	786	363	152	515	271	0·655
Alkali Soil						
Nil	380	288	Nil	288	92	0·760
1	506	382	Nil	382	124	0·755
2	530	360	Nil	360	170	0·715
4	578	324	35	359	219	0·621
6	604	302	68	370	224	0·612
8	631	285	90	375	256	0·594

Effect of Organic Matter : Role of organic matter in retaining the manganese applied to soil has been investigated by two different methods. In the first method soil sample is treated with increasing volume of hydrogen peroxide (1 ml to 20 ml) and then the manganese solution is added. In the second method the soils used were first treated with 20 ml of H_2O_2 and then varying amounts of humus (extracted from the black soil used in the study) have been added.

The gradual oxidation of organic matter by hydrogen peroxide results in a decreased retention of manganese (table-5). However the effect in the case of alkali soil is insignificant. In case of the red soil retention decreases only upto an addition of 5 ml of H_2O_2 but when the H_2O_2 added is increased beyond 5 ml the retention shows an increase, the amount of Mn thus retained, however remains less than the amount retained by the original soil. The exchangeable and reducible forms of manganese decrease in the case black and red soils with increase in the amount of H_2O_2 whilst in the case of the alkali soil exchangeable manganese decreases but the reducible manganese increases.

TABLE 5

Effect of gradual destruction of Organic matter on Mn^{++} retention

Concentration of Mn added = 1100 ppm.

ml. of H_2O_2 used for 5 gm of soils	R	Forms in which Mn^{++} in retained (ppm) E	r	A	F	A/R
Black Soil						
Nil	985	604	174	778	207	0·78
1	994	540	136	676	318	0·67
5	960	491	99	590	370	0·62
10	941	459	84	543	398	0·60
15	932	459	88	547	385	0·60
20	925	450	96	546	379	0·60
Red Soil						
Nil	704	484	75	559	149	0·80
1	502	302	32	334	168	0·66
5	460	332	30	362	98	0·78
10	480	346	30	376	104	0·78
15	503	366	32	398	105	0·79
20	549	374	35	409	140	0·75
Alkali Soil						
Nil	1088	372	432	804	284	0·73
1	1088	334	503	837	251	0·76
5	1084	308	490	798	286	0·74
10	1083	308	477	785	298	0·73
15	1081	262	508	770	311	0·71
20	1081	235	518	753	328	0·79

The addition of humus to the soil which was depleted of its organic matter by 20 ml H_2O_2 results in increased retention of manganese (Table 6). Exchangeable manganese in both the soils shows an increase with increase in the humus added whilst the reducible manganese tends to decrease at higher percent of humus added. Fixed form of manganese increases with increase in humus added to the soils.

Conclusion

When Mn^{++} is added to different soils, it is retained by them in varyirg amounts depending upon their pH, total carbonates and organic matter contents. Most of the retained Mn is found to exist mainly in the exchangeable and reducible forms whilst the rest may be considered to be in the fixed form.

TABLE 6

Effect of addition of Humus on retention of Mn by Organic matter-free soils

Concentration of Mn added - 1100 ppm.

% humus added	R	Forms in which Mn is retained (ppm) E	r	A	F	A/R
Black Soil						
Nil	920	456	95	551	369	0·60
1	932	468	95	463	369	0·60
1·5	936	476	89	565	371	0·60
2·0	940	484	83	567	373	0·60
4·0	950	500	81	581	369	0·61
Red Soil						
Nil	536	357	41	398	137	0·75
1	561	398	41	439	122	0·78
1·5	573	406	36	442	131	0·77
2·0	593	414	31	445	148	0·75
4·0	615	430	27	457	158	0·74

Any Mn that exists in the exchangeable state in the soil after $MnSO_4$ addition is bound to have entered the exchange complex of the soil through the base exchange and points out a state in which added Mn^{++} ions have suffered no change.

However the reducible form of Mn denotes a form of Mn which exists in soils as higher oxides of Mn (such as MnO_2, Mn_3O_4 etc.) which are partially affected by 0·2% quinol in ammonium acetate solution. As appreciable proportion of retained Mn is accounted for by the detection of such a form in soils, it is logical to conceive that added Mn ions have been oxidized so as to attain a higher oxidation state. It requires the presence of oxidizing agents and higher pH values. The soils used which vary from almost neutral to alkaline pH values and the oxidizing agents present may be entrapped oxygen, and ferric ion etc. of the soil. However, the soils contain reducing agents as well-most prominent being the organic matter of the soil. Hence the conversion of Mn^{++} to higher oxidation states is governed by two opposing forces which lead to variable amounts of reducible manganese in the soils after $MnSO_4$ has been added.

The rest of the retained Mn, (not accounted for by E and r) is to be sought for in the fixed state. The conversion of Mn^{++} to a fixed state appears to be favoured by higher pH values, as a maximum fixation of Mn^{++} is observed in the alkali soil. This is further supported by changing the pH of the soils where it is observed that fixed form decreases with the decrease in pH levels in the same soil.

When soils were treated with HCl, carbonates were destroyed and the exchange positions were occupied mainly with H^+ ions, consequently the pH is lowered. Such an unsaturation brings about a decrease in the Mn^{++} retention. The unsaturation of the soil keeps a greater percentage of retained Mn^{++} in exchangeable form. It shows that in the absence of free $CaCO_3$ and in the presence of acidic exchange complex, more and more of applied magnagese will be held in exchangeable positions. It is also supported by the addition of $CaCO_3$ to the same HCl-treated soils. As the percent of $CaCO_3$ added to the soil is increased, retained manganese tends to increase which shows that $CaCO_3$ is responsible for the retention of manganese. But the retained manganese is mostly in the form of

reducible manganese, the exchangeable manganese exhibits a decreasing trend with increased additions of free $CaCO_3$.

Organic matter is responsible for the retention of manganese mostly in the exchangeable form. From the results it is also evident that addition of humus leads to reducing conditions in the soils so that the reducible form of manganese is on decrease. Some of the added Mn^{++} may form the organic complexes because fixed form of the manganese increases with addition of humus to the soils.

Summary

The present studies were undertaken in order to find out the fate of manganese applied as manganese sulphate to three different groups of soils of Uttar Pradesh *i.e.* the black, the red and the alkali soils. For clarification of the role of organic matter, carbonate and pH in retention of manganese supplicated externally, retention studies were carried out in absence as well as in presence of increasing doses of calcium carbonate and organic matter. The effect of pH on retention of manganese has been worked out by lowering the equilibrium pH of the soil and solution mixture. In all the cases estimations of exchangeable and reducible forms of manganese have been made.

The observations clearly indicate that alkali soil retains almost all the applied manganese, whilst the red soil retains the least, but black soil occupying an intermediate position. In presence of the increasing doses of calcium carbonate and humic acid although the retention shows an increasing trend in both the cases, the exchangeable manganese has been found to decrease in former case but it increases in the latter case. The reducible form of manganese increases in the case of calcium carbonate addition but in the presence of humic acid it decreases. The lowering of equilibrium pH results in gradual decrease in Mn-retention.

References

1. Beckwith, R. S. Studies of soil manganese. 1. The use of disodium calcium versenate for the extraction of divalent manganese from soils. *Australian J. Agr. Research*, **6** : 299-307, 1955.
2. Beckwith, R. S. Metal complexes in soils. *Australian J. Agr. Research*, **6** : 685-689, 1955.
3. Bioschot, P., Duroux, M. and Stylvenstre, G. Studies on the fixation of iron and manganese by calcareous soils. *Agronomique*, 1-5, 1950.
4. Christensen, P. D., Toth, S. J. and Bear, F. E. Status of soil manganese as influenced by moisture, organic matter and pH. *Soil Sci. Soc. Amer. Proc.*, 273-282, 1950.
5. Heintze, S. G. Studies on soil manganese. *J. Soil. Sci.*, **8** : 273-300, 1957.
6. Heintze, S. G. and Mann, P. J. G. A study of the various fractions of manganese of neutral organic soils. *J. Soil. Sci.*, **2** : 234-242, 1957.
7. Jackson, M. L. Soil Chemical Analysis. *Asia Publishing House*, 1962.
8. Jones, L. H. P. A note on the reduction of manganese in neutral to alkaline soils. *Trans. Intern. Soc. Soil Sci. Joint Meeting Comm. II and Comm. IV* **2** : 164-166, 1952.
9. Leeper, G. W. The forms and reactions of manganese in the soil. *Soil Sci.*, **63** : 79-94, 1947.
10. Page, E. R. Studies in soil and plant manganese 1. The relation of soil pH to manganese availability. *Plant and Soil*, **16**(2) : 247-257, 1962.
11. Passioura J. B. and Leeper, G. W. Available manganese and X-hypothesis. *Agrochemica*. **8** : 81-90, 1963.
12. Sherman, G. and Harmer, P. M. Manganese deficiency of oats on alkaline organic soils. *J. Am. Soc. Agron.*, **33** : 1082-1092, 1941.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968.

Migration of Plant Nutrients through soil

By

C. DAKSHINAMURTI

Head of the Division of Agricultural Physics, Indian Agricultural Research Institute, Delhi-12

Soil, the store house of plant food, not only serves as a base to the plant to stand erect on it but also permits the healthy nutrient-sucking roots to spread and properly develop under favourable conditions of soil moisture and soil air. In spite of good seeds, sufficient irrigation water and right type of fertilizers, it is often observed that the crop production is not intensive. This is attributed to the rate limiting steps in ion uptake by plants from soil (1). It is thus apparent that the term soil fertility should be taken in a broader sense than hitherto considered only from the chemical point of view.

Effective pore space

In a heterogeneous multi component system, such as soil, equilibria will exist or tend to be attained between the solid and liquid phases. Although it is believed that the reactions between ions at the solid surface and in solution are usually rapid, a possible rate-limiting step is the transfer of ions through the micropores into larger pores in the soil system. The effective porosity thus seems to be more important than the actual porosity of the soil system (2). This can be worked out in soils by either electrical conductivity or ionic diffusion methods.

Mass flow and diffusion

There are two main processes for the movement of the fertilizer ion *viz.*, mass flow of water and diffusion of the ions (3, 4). It is difficult to distinguish between these two phenomena unless the exact model is defined. By far mass flow is significant in transporting the nutrient ion. When once the mass flow ceases, ionic diffusion alone becomes effective. Mass flow though considered as a laminar flow through soils should be distinguished from true laminar type. Here, a special factor, dispersion, should be considered ; by dispersion is meant the disturbances which occur in the flow pattern due to geometrical factors. In most theoretical approaches this effect is accounted for in the diffusion coefficient. This is not correct as the higher the rate of the flow the more important is the dispersion factor as compared to the diffusion factor.

Diffusion of nutrient ions through soils, though of great importance in fertilizer studies, seems to have been severely limited by the absence of a body of coherent data of diffusion coefficients in known framework of systems. The effect of diffusion is so conspicuous that a certain amount of ion that would diffuse into a sandy loam soil at a suction pressure of 7·5 cm. would take about three days and twenty three days respectively for suction pressures of 13·5 and 25·1 cm. applied. This rapid decrease in the amount of ion diffused with increase in the suction applied is important in understanding the fertilizer movement in placement experiments (5).

Soil structure

Migration of nutrient ions is severely limited in most of the Indian soils where problems of compaction, inadequate aeration and undesirable soil moisture relationships for the growth of plants are wide spread. These undesirable physical factors associated with high soil temperatures seriously affect plant growth even in soils potentially fertile.

All these factors can be grouped under a broad heading soil, structure (6). It is most desirable to apply a reliable technique to estimate the relative structural status of the soils and evaluate the effectiveness of soil amendments in improving the structure. A good soil structure permits adequate migration of soil water and air through its pores. The movement of water is measured by the hydraulic conductivity of the system. A comparison of a large number of structural indices of soil indicated that hydraulic conductivity at minimum compacted bulk density works out to be significant enough to distinguish the structural differences from layer to layer in the root zone of crops (7). Different management practices and their relative effectiveness in developing the soil structure require to be worked out with a view to attaining the optimum structural status, a must for intensive cultivation.

Subsoil water

The root zone gets its moisture both from the water that infiltrates from the top layers and the water that rises up through capillary action from the subsoil layers. It is this water which contains the nutrient ions that are sucked by the plant roots. It is realised in all modern practices of agriculture that the maintenance of proper soil structure in the top layers and an adequate moisture regime in the subsoil, will be most beneficial in keeping the root zone sufficiently wet to supply the nutrient ions for a proper and healthy growth of the root system resulting in an intensive crop yield. Significant correlations between subsoil moisture and wheat yields were observed (8).

Modern technology

Several modern physical techniques such as neutron moisture meter, gamma ray density probe and computerised weather models are being applied today to understand the optimum physical conditions conducive to economic and effective use of fertilizers for intensive crop production. Radioactive isotopes are being increasingly used for solving several problems of fertilization in field experiments as well as in the long term programme of soil fertility research on the fundamental question of plant nutrient supply and movement (9).

References

1. Limiting steps in ion uptake by plants from soil. *Technical Report series No.* 65. *International Atomic Energy Agency, Vienna,* 1966.
2. Dakshinamurti, C. Effective Porespace measurements in porous media by ionic diffusion. *Soil Science,* **88** : 209-212, 1959.
3. Dakshinamurti, C. Ionic migration in soils and clays. *Techn. Rep. Ser.* 48 ; Plant nutrient supply and movement, 57–72. *International Atomic Energy Agency, Vienna,* 1965.
4. Dakshinamurti, C. and Mansharamani, N. Role of mass movement and ionic diffusion in ionic migration through soils. *Techn. Rep. Ser.* 65, Limiting steps in ion uptake by plants from soil, 46–56. *International Atomic Energy Agency, Vienna,* 1966.
5. Dakshinamurti, C. Ionic diffusion in soil. *Proc. Nat. Acad. Sci. India* **24** (1) : 25–27, 1955.
6. Dakshinamurti, C. Soil structure Part I (Basic concepts) Part II (Plant growth) U. G. C. Lectures delivered at Hissar, Punjab University. *J. Post. Grad. School, IARI* (in press), 1966.
7. Dakshinamurti, C. and Pradhan, C. Hydraulic conductivity as an index of soil structure. *Soil Sci. and Plant Nutrition, Japan,* **12** (4) : 8–12, 1966.
8. Thomas, J. R., Army, T. J., and Cox, E. L. Relationship of soil moisture and precipitation to spring wheat yields in the northern Great Plains. *Production Research Report No.* 56. *U. S. Dept. of Agri.* 1–24, 1962.
9. Plant Nutrient Supply and Movement. *Technical Report Series No.* 48. *In ernational Atomic Energy Agency, Vienna,* 1965.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968

Infrared curves of fertile and infertile soils

By

S. K. DE

Department of Chemistry, University of Allahabad

De[1] (1966) was the first to show that the peaks in the infrared curves of a few Indian soil samples could be interpreted in terms of some properties of the latter.

In this paper, some preliminary observations on the IR-peaks of some Indian soil samples which can be ascribed to their fertility measure, have been reported.

Experimental

Details of the experimental procedure adopted have already been given elsewhere (De[1], 1966).

The soil sample (particles lesser than 2μ) is transformed into a KBr–mull and placed in the sample holder of a Perkin-Elmer Infrared Spectrophotometer for obtaining the IR-curve of the sample. The bigger undecomposed particles must be removed before pulverisation of the soil sample as those may cause damage to the mull die and a reproducible IR-curve may not be obtained. Nujol-mull technique was not found useful as the IR-spectra of Nujol oil was found to overlap most of the IR-curve region assigned to the base exchange capacity of the soil.

Since it is observed that a characteristic spectra of a soil sample can be obtained in the wavelength range, 2μ to 15μ, the IR-curves of the soil samples above 15μ was not considered.

Results and Discussion

It is well-known that a fertile soil may be defined as the one which has the potentiality of supplying nutrient elements in proper forms and quantities for the completion of the life-cycle of a plant. A soil is said to have active or kinetic fertility when it has an appreciable measure of easily accessible forms of food materials such as the exchangeable and soluble nutrients. In a potentially fertile soil the nutrients are present in less easily extractable form in organic matter and in primary and secondary minerals. An agriculturally-important land is, therefore, one which has more kinetic fertility than potential fertility and the so-called infertile soils or the agriculturally less-important soils have negligible kinetic fertility. In other words, with an increase in kinetic fertility the soils are expected to be rich in clay fractions which contain less weatherable clay minerals having in most cases complexation with decomposed organic materials.

It is well-hnown (Grim[2], 1953) that clay minerals give characteristic infrared absorbtion curves in the wavelength range 2μ to 15μ. De[1] (1966) has recently observed that in this wavelength range, the clay-humus complex also give a notable IR-absorption peak (*Table* 1), and that sharp IR-absorption peaks indicate that the finer fraction of the soil has perfect clay minerals with negligible proportion of the less resistant weatherable primary or secondary minerals which give no characteristic and less-differentiated broad absorption peaks in the said wavelength

TABLE 1

Characteristic peaks in the I. R. absorption curves of kinetically and – potentially – fertile and infertile soils

Soil	Fertility	Wavelength (μ)					
		Unbonded and bonded water	Base exchange capacity	Si – O	Al – O	pH	Clay-humus Complex
1. Alluvial, Allahabad	Kinetically fertile	2·90	5·00 – 7·40	9·70	10·00	10·95	12·40, 12·75, 14·20, 14·50
2. Highly Acidic, Thotapally	,,	2·95	5·00 – 7·65	8·95 – 9·40	10·10	11·20	12·60, 12·90, 14·40, 14·80
3. Red, Ranchi	,,	2·70	4·80 – 7·40	9·10	9·90 – 10·30	11·00	12·35, 12·75, 14·10, 14·35
4 Black, Jhansi	,,	2·60	5·00 – 7·90	8·80	9·90	—	12·20, 12·80, 14·40, 15·00
5. Grey, Ajmer	Potentially fertile	2·90	6·00 – 6·90	8·70	9·00 – 10·50	—	12·30, 12·90, 14·20
6. Alkali, Allahabad	,,	2·50	5·10 – 6·80	8·60	9·80	—	12·00, 12·60, 14·25
7. Hill, Garhwal	,,	3·00	5·20 – 6·10	8·10	10·30	11·10	12·35, 12·80, 14·00
8. Bundelkhand Type I, U. P.	,,	2·85	5·10 – 5·70	6·70	9·60	—	—
9. Rocky-ridge, Bundelkhand	Infertile (1)	2·65	5·10 – 5·80	9·00	11·80	—	—
10. Rocky-ridge, Bundelkhand	Infertile (2)	2·65	4·80 – 5·25	8·70	11·45	—	—

TABLE 2

Percent composition of the soil samples

Constituents	Soil Sample									
	Alluvial, Allaha-bad	Highly Acidic, Thota-pally	Red, Ranchi	Black, Jhansi	Grey, Ajmer	Alkali, Allaha-bad	Hill, Garhwal	Bundelkhand Type I (U. P.)	B. D. T. I Rockyridge (1) (U. P.)	B. D. T. I Rockyridge (2) (U. P.)
HCl – insoluble	88·82	82·67	82·12	73·45	80·22	84·82	75·99	82·11	85·11	86·12
Sesquioxide	8·78	8·83	12·14	15·94	34·08	9·31	11·50	11·90	9·82	9·73
Fe_2O_3	4·31	4·65	4·25	5·67	10·78	4·73	3·41	3·62	3·71	3·61
Al_2O_3	4·46	4·04	7·87	10·24	22·24	4·36	8·22	8·31	6·10	5·97
CaO	3·32	0·35	0·48	2·21	1·56	1·34	1·23	1·10	0·31	0·25
MgO	1·61	0·39	0·45	2·62	2·48	2·21	0·88	1·12	0·13	0·15
K_2O	1·72	0·68	2·14	1·83	0·78	0·62	0·61	0·60	0·10	0·11
P_2O_5	0·17	0·072	0·018	0·041	0·101	0·11	0·061	0·057	0·021	0·035
pH	8·2	4·5	6·2	8·9	10·1	9·7	6·9	7·5	7·8	8·1
Organic C	0·10	3·11	0·29	0·15	0·13	0·183	2·92	0·13	0·11	0·10
Nitrogen	0·071	0·332	0·031	0·051	0·051	0·038	0·16	0·051	0·021	0·013
C/N	15·4	9·3	9·3	2·9	2·5	4·8	18·2	2·5	5·23	7·69
B. E. C. (m.e.%)	26·21	31·24	19·81	45·25	12·82	11·22	6·82	9·08	2·05	2·14
Ex. Ca (,,)	21·41	6·12	15·84	25·23	3·28	2·10	3·20	4·12	0·28	0·28
Ex. Mg (,,)	3·11	13·12	3·68	18·13	3·85	1·48	1·78	2·21	0·58	0·48
Ex. K (,,)	0·82	0·63	0·18	1·24	0·25	0·22	0·88	0·21	0·75	0·85
Ex. Na (,,)	0·84	—	—	1·82	5·08	7·22	—	2·52	0·10	0·51
Coarse Sand	1·58	13·56	8·24	7·88	65·45	5·12	14·51	70·10	84·11	83·24
Fine Sand	44·72	31·35	44·12	31·32	26·22	27·98	45·52	21·01	14·23	13·25
Silt	39·42	28·80	21·14	33·45	3·92	47·92	20·61	2·01	1·35	1·28
Clay	14·01	23·08	26·24	25·12	4·54	14·18	11·22	6·80	0·21	1·34

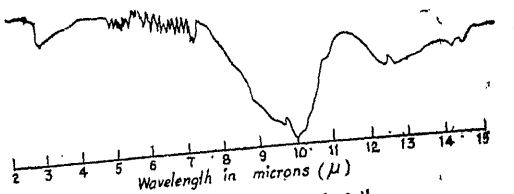


Fig. 1. Infrared Spectra of Alluvial Soil (Kinetically fertile)

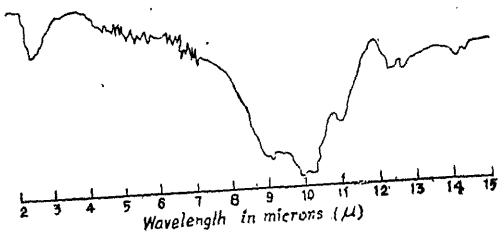


Fig 2 Infrared Spectra of Red Soil (Kinetically fertile)

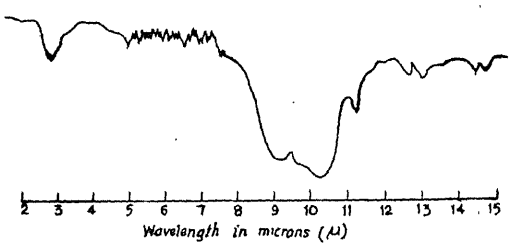


Fig 3 Infrared Spectra of highly Acidic Soil (Kinetically fertile)

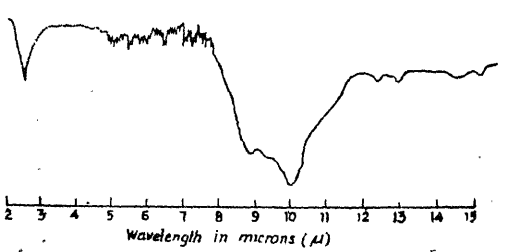


Fig. 4. Infrared Spectra of Black Soil (Kinetically fertile)

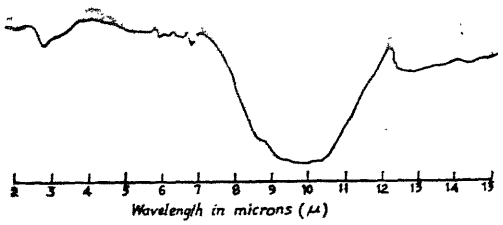


Fig. 5 Infrared Spectra of Gray Soil
(potentially fertile)

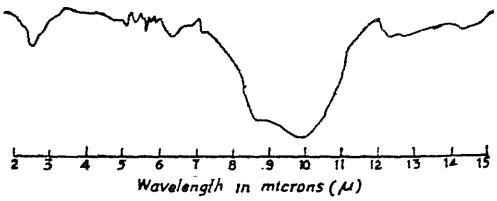


Fig. 6 Infrared Spectra of Alkali Soil
(potentially fertile)

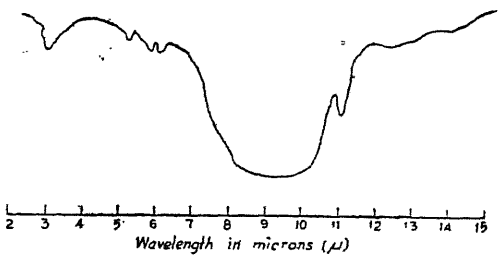


Fig. 7. Infrared Spectra of Hill Soil
(potentially fertile)

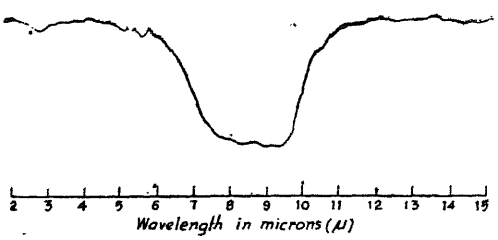


Fig. 8. Infrared Spectra of Bundelkhand Type I Soil
(potentially fertile)

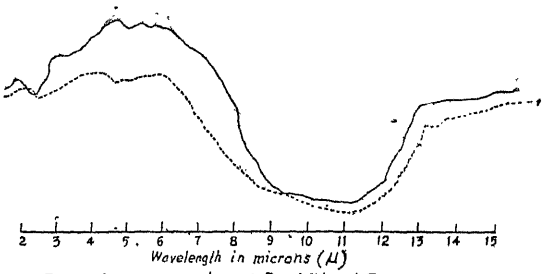


Fig 9 *Infrared Spectra of Bundelkhand Type I Rocky-Ridge Soil (infertile soil)*

range. It is thus obvious that in this wavelength range, if the absorption peaks in the IR-curve of the soil are sharp and numerous (Fig. 1 to 4), these are definitely indications of kinetic fertility and as the infrared absorption peaks of a soil decrease in sharpness and number (Fig. 5 to 9), it may be said to possess more of potential fertility than kinetic fertility. The absorption peaks in the IR-curve of an infertile soil is, therefore, expected to be very broad and few in number (*Table* 1) and mutually less differentiated (Fig. 9).

Summary

Some preliminary observations on the IR-peaks of some Indian soil samples which can be ascribed to their fertility measures, have been reported. The number of IR-peaks in a kinetically fertile soil are at least six and such peaks are generally sharp in nature. A potentially fertile soil has generally four or less than four peaks in its infrared absorption curve. The infrared absorption peaks for infertile soils are broad, less sharp and less defined.

References

1. De, S. K. *D.Sc. Thesis, Allahabad University*, 1966.
2. Grim, R. E. *Clay Mineralogy. Mc Graw Hill Book Co., Inc.*

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968

Cation exchange capacity of Bihar Soils in relation to Organic matter and pH

By

A. K. SINHA, H. SINHA *and* S. C. MANDAL

Ranchi Agricultural College, Kanke, Ranchi, Bihar

The relation between cation exchange and the availability of many plant nutrients is well recognized. Not only the productivity but also the physical, chemical and biological properties of the soil may be influenced by total exchange capacity and exchangeable cations. The cation exchange capacity (C. E. C.) is involved to an important degree in soil formation and the development of acidity and alkalinity in soils. As a number of soil porperties are dependent on C. E. C., an effort to evaluate it is likely to be helpful in understanding soil management problems. C. E. C. of soils depends on a number of factors, *e.g.* clay minerals, soil reaction, organic matter, temperature, moisture and crops, etc. There is absolute lack of informations on most of these factors and their effects on C. E. C. of Bihar soils. In the present study an attempt has been made to study C. E. C. of these soils in relation to their organic matter contents and pH values and effects of bringing about change in these soil attributes.

Experimental

14 surface soil samples representing sedentary and alluvial soils of Bihar were used for the present investigation. Soils were analysed for their physical, chemical and physico-chemical properties. The texture was determined from their mechanical analysis which was done by International pipette method, while pH was measured in a soil-water suspension ratio of 1 : 25 with a Beckman pH meter. Organic carbon was determined by Walkely and Black method and total N by modified kjeldahl method (Jackson 1958). Normal neutral ammonium acetate method was followed for the determination of C. E. C. and exchangeable cations as described by Jackson (1958). C. E. C. of the soils were also determined after removal of organic matter with 6% H_2O_2, acidic $KMnO_4$ and $K_2Cr_2O_7$ solutions (10 c.c. N $KMnO_4$ or $K_2Cr_2O_7$ solution plus 20 c.c. conc. H_2SO_4). After these treatments, the soils were washed free from acid and C. E. C. were determined. These soils were also brought to pH 7·0 with a saturated solution of $Ca(OH)_2$ or 0·0364 N HCl after equilibrating them for 72 hours in a soil-water ratio of 1 : 10. After decanting of the reacting solution, soils were washed with small quantities of neutral alcohol and C. E. C. determined. Exchangeable Ca,K and Na were determined with a flame photometer. The C. E. C. of the organic matter was calculated from the C. E. C. of the original soil and that after removing the organic matter with H_2O_2.

Results and Discussion

The characteristics of soils are reported in Table 1.

TABLE 1

Soil characteristics

Soils	Texture	Clay %	pH	Org C %	Exch Ca ←m. e. %→	Exch K ←m. e. %→	Exch Na ←m. e. %→	C. E. C. ←m. e. %→
	Alluvial soils							
Raxaul	Loam	24·9	6·1	0·40	6·07	0·19	0·46	14·30
Saharsa	Sandy loam	8·9	8·2	0·19	6·07	0·19	0·62	6·75
Katihar	Sandy loam	18·3	6·3	0·29	2·14	0·25	0·46	8·07
Araria	Sandy loam	8·6	6·0	0·24	2·86	0·25	0·58	5·80
Bikramganj	Sandy clay loam	22·5	5·7	0·45	3·58	0·27	9·37	10·70
Patna	Clay	43·6	8·3	0·47	14·60	0·40	0·58	23·67
Sabour	Loam	18·9	7·3	0·22	2·86	0·34	0·86	11·24
	Sedentary soils							
Gaya	Clay loam	29·1	6·8	0·23	1·07	0·35	0·48	13·45
Nawadah	Sandy clay loam	28·9	7·2	0·14	4·28	0·27	0·48	8·45
Ranchi	Sandy clay loam	31·1	5·7	0·29	2·50	0·44	0·54	7·60
Chiabasa	Sandy loam	10·2	6·2	0·13	1·01	0·18	0·46	3·07
Putida	Clay loam	31·2	8·3	0·87	18·67	0·47	0·62	41·53
Hazaribagh	Sandy loam	15·1	6·1	0·36	0·71	0·35	0·46	4·01
Giridih	Sandy loam	30·1	7·1	0·63	5·71	0·21	1·01	12·22

Texturally the soils were sandy loam to clay which varied from 8·6-43·6% in clay, 5·7–8·3 in pH and 0·13–0·87% in organic carbon. The C. E. C. of these soils varied from about 4 to 40 m.e.%, there being hardly any difference between alluvial and sedentary soils. The higher values were generally associated with the heaviour texture of soils. C. E. C. was found signficantly correlated not only with the clay content but also, the relationship between C. E. C. and organic matter was highly significant, co-efficients of correlation being 0·6178 and 0·8194 respectively. These results correspond with those of Pratt (1957). The highest values of C. E. C. and organic carbon in Putida soils point to its exceptional nature from that of soils generally occurring in this area. The Putida soil has been found to resemble with black cotton soil in respect of colour, organic matter content, physical consistency and chemical characteristics (Sinha and Bhattacharya, 1964). The high C. E. C. of this soil indicate that the dominant clay minerals in this soil would be other than kaolinite which is usually found in the soils of this area. Of the exchangeable cations, Ca occur in highest amounts and exchangeable Na was more than exchangeable K in all soils.

Effect of removal of organic matter of soils

Oxidation with H_2O_2 : The treatment of soils with H_2O_2 resulted in considerable decrease in C. E. C. of soils (Table 2).

TABLE 2

C. E. C. of soils on treatment with various oxidising agents

Soils	No treatment	H_2O_2	$KMnO_4$	$K_2Cr_2O_7$	H_2O_2	$KMnO_4$	$K_2Cr_2O_7$
	← m. e. % →				← % decrease →		
	Alluvial soils						
Raxaul	14·30	10·58	6·15	6·38	26·0	56·9	55·3
Saharsa	6·75	5·76	2·12	1·80	14·5	66·8	73·4
Katihar	8·07	5·96	5·95	2·35	26·0	26·1	70·8
Araria	5·80	4·80	1·38	1·61	17·2	80·3	85·3
Bikramganj	10·70	12·01	5·13	5·64	12·2*	51·5	47·2
Patna	23·67	23·50	9·77	10.70	0·7	58·6	54·9
Sabour	11·24	8·17	3·89	4·39	27·3	65·3	60·8
	Sedentary soils						
Gaya	13·45	13·28	7·40	8·75	1·3	44·2	34·4
Nawadah	8·45	7·93	5·09	5·78	6·0	39·7	31·5
Ranchi	7·60	8 75	5·97	5·83	15·1*	21·3	23·2
Chiabasa	3·07	2·39	2·62	2·90	21·9	8·1	5·2
Putida	41·53	37·12	15·74	15·01	10·6	62·1	61·2
Hazaribagh	4·01	3·74	2·95	3·37	6·5	26·2	18·2
Giridih	12·22	11·03	7·27	8·71	9·6	40·3	28·7

*indicates increase

Percent decrease of C. E. C. of soils due to H_2O_2 varied from 0·7 to 27·3, Bikramganj and Ranchi soils were exceptions as they recorded a rise in C. E. C. Bartlett *et al*, (1937) obtained a fall of 80–90% of C. E. C. in Maryland soils on treatment with H_2O_2. Sasaki (1960) also reported a decrease in C. E. C. due to the destruction of both organic and inorganic constituents of soils. In the present investigation, the increase in C. E. C. of Ranchi soil may be due to the partial destruction of oxides of Fe and Al leading to the reduction of aggregates formed by these oxides. According to Dion (1944), hydrated Fe_2O_3 reduces the C. E. C. by clogging action, hence a destruction of this oxide with H_2O_2 will expose the exchange sites. The destruction of organic ions clogging the exchange sites according to Hendricks (1944) may be another explanation, particularly in Bikramganj soils. Recently Sasaki (1960) showed that due to the treatment of soils with H_2O_2 new inorganic minerals are fromed and a higher exchange capacity may be expected.

Oxidation with $KMnO_4$ and $K_2Cr_2O_7$: As apparent from Table 2 oxidation of the soils with more strong oxidising agents like acidic $KMnO_4$ and $K_2Cr_2O_7$ resulted in a drastic decrease in C. E. C. of all soils. The decrease in C. E. C. varied from 8·1–80·3% in case of $KMnO_4$ and from 5·2–85·3% in case of $K_2Cr_2O_7$. Generally the reduction in these cases were of the same order and several times more than that with H_2O_2. The drastic decrease in C. E. C. may be attributed to the destruction of both organic and inorganic fractions of soils. Not only these

stronger oxidising agents might have caused oxidation of organic matter more efficiently, but also the strong acid treatment might have attacked the clay micelle and led to its destruction resulting in the reduction of C. E. C.

C. E. C. of organic and mineral fractions of soils : From the C. E. C. values obtained from soils before and after oxidation of organic matter with H_2O_2, (Table 2) the C. E. C. of organic and mineral fractions along with their contributions to soils have been worked out as reported in Table 3.

TABLE 3

C. E. C. of organic and mineral fractions of soils

Soils	Org. matter	Mineral	Contribution of org. matter	Mineral based on clay %	Contribution of minerals	Contribution of org. matter	Dominant clay minerals*
	← m.e. % →				% of total C. E. C.		
	Alluvial soils						
Raxaul	541	10·6	3·7	42·2	74·0	26·0	Illite & Kaol
Saharsa	300	5·8	1·0	65·2	85·8	14·2	,,
Katihar	422	6·0	2·1	32·8	74·3	25·7	,,
Araria	294	4·8	1·0	56·0	82·4	17·6	,,
Patna	21	23·5	0·2	54·0	95·0	5·0	,,
Sabour	808	8·2	3·1	43·4	73·0	27·0	,,
(Mean)	389	9·8	1·8	49·0	80·7	19·2	
	Sedentary soils						
Gaya	250	13·3	0·2	45 7	98·7	1·3	Illite & Kaol
Nawadah	217	7·9	0·5	29·2	93·9	6·1	Do
Chiabasa	209	2·4	0·7	23·5	77·9	22·1	Kaol & Illite
Putida	294	37·2	4·4	120·0	89·4	10·6	Kaol & Mont.
Hazaribagh	43	3·7	0 3	24·7	93·3	6 7	Kaol & Illite
Giridih	110	11·0	1·2	36·7	90·3	9 7	Do
Mean	189	12·6	1·2	46 6	90·6	9·4	

*Prasad *et al* (1966)

The C. E. C. of organic matter varied from about 20–800 m.e.% with a mean value of 389 m.e.% in alluvial soils while that in sedentary soils, the variation was between about 40-300 m.e.% with a mean value of 189 m.e.%. From these figures it appeared that the organic matter of alluvial soils, in general, had greater exchange capacity than that of sedentary soils. Hosking (1948) and Siuta (1961) reported C. E. C. of organic matter as about 500–600 m.e.% in soils. In the present study, the contribution of organic matter towards C. E. C. of soils varied between about 0·2–4·0 in both the type of soils. There was however, a difference in the mean values which were about 1·8 and 1·2 m.e.% in alluvial and sedentary soils respectively. In alluvial soils of Bihar, organic matter contributed from

5-27% with a mean value of 19·2% of C. E. C. while the corresponding figures in sedentary soils were 1·3-22·1% with mean value of 9·4%. Minerals accounted for about 80% in alluvial soils about 90% of exchange capacity in sedentary soils. The data of Endredy and Quagraine (1960) indicate that organic matter accounted for less than 10 to more than 60% of exchange capacity in Ghana soils. According to Siuta (1961), 6-44% of total exchange capacity of soils could be attributed to organic matter when humic acids were extracted with 0·1N NaOH following decalcification. The exchange capacities of mineral part obtained by referring the actually estimated exchange capacity of H_2O_2 treated soil to the clay content appeared high for these soils. This may be due either to the undetermined presence of other clay minerals (illite and montmorillonite) in the clay fraction or to the exchange capacity of the coarser fraction, which particularly in soils derived from micaceous schists, can be considerable.

Effect of neutralising soils

Considerable decrease in C. E. C. of soils were observed on bringing the soils to pH 7·0 from both sides of the pH scale (acid or alkaline). The results are reported in Table 4.

TABLE 4

C. E. C. of soils adjusted to pH 7·0

Soils	Initial pH	C. E. C. m. e. % at Initial pH	C. E. C. m. e. % at pH 7·0	% decrease	Rate of decrease per unit pH
	Alluvial soils				
Raxaul	6·15	14·30	7·31	48·9	8·6
Saharsa	8·25	6·75	3·48	48·5	2·6
Katihar	6·30	8·07	4·78	40·6	4·7
Araria	6·05	5·80	2·69	53·6	3·3
Bikramganj	5·70	10·70	7·83	26·8	2·2
Patna	8·30	23·67	23·85	0·7*	0·1
Sabour	7·30	11·24	7·05	37·3	14·0
	Sedentary soils				
Gaya	6·80	13·45	9·63	29·1	19.0
Nawadah	7·20	8·45	3·30	60 9	25·7
Ranchi	5·72	7·60	3·56	53·0	3·2
Chaibasa	6·20	3·07	2·17	29·0	1·1
Putida	8·30	41·53	36·09	13·1	4·2
Hazaribagh	6·10	4·01	2·17	45·6	2·0
Giridih	7·10	12·22	8·40	31·3	38·2

*indicates increases.

Near neutral to alkaline soilss howed a decrease C.E.C. from 29·1 to 60·9 m.e.%, while a reduction of 26·8 to 53·0 m.e.% was recorded in acid soils when brought to pH 7·0. Raising the pH of soils generally results in an increase of C.E.C. as reported by several workers including Hosking (1948) and Schofield (1949) but none of the soils used in the present study showed this. Yoshida (1956), however,

showed that the adsorption of cations decreased with decreasing pH. According to Cho (1959), the C. E. C. of illite was greatly reduced particularly by Ca^+ and by H^+ ions. These findings are in agreement with the results of the present investigations. Deterioration of soil structure due to break down of Fe and Al in clay on acid treatment, attack of acid on soil organic matter and inactivation of exchange sites by H^+ ions due to neutralising OH^- groups present on exchange sites of humus have been advanced as possible causes for the decrease in C. E. C. of soils. But such high reductions of C. E. C. on treatment of soils with very small amounts of acid as used in the present study is not quite understandable. The rate of decrease of C. E. C. per unit of pH varied from 0·1-14·0 with a mean value of 5·1 m.e.% in alluvial soils while in sedentary soils the corresponding variation was from 1·1-38·2, mean value being 13·2 m.e.%. It was not related to the mineral type or the magnitude of the C. E. C. It is to be noted, however, that the higher rate of decrease of C. E. C. was associated with the near neutral soils (pH 6·8–7·3).

Summary

Cation exchange capacity (C. E. C.) of Bihar soils varying between about 4 to 40 m.e. percent was significantly correlated with their clay and organic matter contents, the respective co-efficients of correlation being 0·6178 and 0·8194. Removal of organic matter by various oxidising agents resulted in appreciable reduction of C. E. C. of soils. This varied from about 1-25% with H_2O_2, 8–80% with $KMnO_4$ and 5–85% with $K_2Cr_2O_7$ solution. The mean C. E. C. of organic matter of alluvial and sedentary soils were found to be about 400 and 200 m.e. percent respectively suggesting a difference in its quality. This was also apparent from the fact that the organic matter contributed about 20% and 10% of the total exchange capacity in alluvial and sedentary soils respectively, eventhough there was practically no difference in their organic matter contents. Adjusting the pH of acidic and alkaline soils to 7·0 resulted in the reduction of C. E. C. to about 40%. The mean rate of decrease of C. E. C. per unit pH was about 5 and 13 m.e. percent in alluvial and sedentary soils respectively. This was, however, not related to the mineral type or the magnitude of the C. E. C.

References

Bartlett, *et al.* *Soil Sci*, **44** : 123, 1937.
Cho, C. M. *Bibliography*, C. B. S. England, 1959.
Dion, H. G. *Soil Sci*, **58** : 411, 1944.
Endredy, A. S. De and Quagraine, K. A. *Trans. 7th Int. Congr. Soil Sci.*, **2** : 312, 1960.
Hendricks, S. B. *J. Phys. Chem*, **45** : 65, 1944.
Hosking, J. S. *Soils and Fert.*, **11** (6) : (1730-31) 369, 1948.
Jackson, M. L. *Soil Chemical Analysis*, Constable & Co., Ltd. London, 1958.
Prasad, R. N. *et al.* *J. Indian Soc. Soil Sci.*, (In press)., 1966.
Pratt, P. F. *Soil Sci.*, **83** (2) : 85, 1957.
Sasaki, Seuchi. *Soil Sci. and Plant Nutri.*, **6** (3) : 106, 1960.
Schofield, R. K. *J. Soil Sci.*, **1** : 1, 1949.
Sinha, S. D. and Bhattacharyya, P. B. *National Institute of Sciences of India Bul.* No. 26, 37, 1964.
Siuta, J. *Soils and Fert.*, **24** (3) : 176, 1961.
Yoshida, M. *J. Sci. Soil, Tokyo*, **27** : 241, (c.f. Bibliography, C. B. S., England), 1956.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968

The Effect of Soil Compaction on Plant Growth and Nutrient Uptake*

By

G. SRIRAMAMURTY

Officer-in-Charge, Tobacco Research Station, Pusa (Bihar State)

Introduction

Soil productivity is often limited by soil physical properties. When crop yields go down despite the use of proper and adequate fertilizers and supply of optimum moisture etc., the physical condition of the soil is believed to become the limiting factor. Compactness of the soil is one such physical condition wherein the downward movement of water or the downward extension of roots is limited. And, adoption of new and intensive soil management systems, rapid changes in fertilizer practices, and use of heavy implements are some of the factors that contribute to the bad physical condition, mainly through compaction of the soil. The primary effects of soil compaction on plants may be divided into the effect on (*a*) germination and seedling emergence, (*b*) root and shoot growth and yield and (*c*) nutrient uptake of plants.

Review of Literature

Wollny (quoted from 2, p. 5) was perhaps the first to study the effect of compaction on soil physical properties. Various workers have subsequently investigated many aspects of soil compaction both in the field and the laboratory. Detailed reviews have since been published by Lutz (11), Raney *et al* (15), Waiters and Simonson (22) and Wiersma (21). Brind (5) reviewed some German and Austrian work on soil compaction and fertility.

Poor root growth in compacted soils may be due to lack of moisture or oxygen, mechanical impedance or low nutrient content as in some of the genetic hard pans (15). Veihmayer & Hendrickson (19, 20) found that roots of sunflower plants failed to penetrate soils with apparent density of 1·8 g/cc. in case of loams, 1·75 g/c.c in sandy soils and 1·46 to 1·63 g/c.c in case of clays. The stand of sugarbeets was very poor (3) in soils in which the noncapillary porosity was less than two percent. Similar trend was noticed by Smith & Cook (16). Crossby (6) reported that permanently compacted subsoils confine rooting mainly to the superimposed soil horizons, with the degree of confinement depending on the degree of compaction. Bertrand & Kohnke (4) reported that corn roots did not penetrate a compact subsoil at a bulk density of 1·5 g/cc.

Winters and Simonson (22) concluded that mechanical difficulties in root growth coupled with restricted aeration provide adequate reason for the limited penetration by most plant roots.

De Roo and Weggoner (7) reported that root penetration of potatos was inhibited at plough depth by the hard pan induced by normal tillage. Meredith and Pattrick (12) observed decreased root penetration into artificially packed cylinders as soil compaction increased. Trouse and Humbert (18) established critical soil bulk densities for rooting of sugarcane for the principal soils of Hawaii.

*Material forms part of Ph.D. thesis submitted to Kansas State University, U. S. A.

Lawton (10) presented an extensive review of the work done on the effect of compaction, aeration and moisture on the absorption of nutrients. Several workers reported lower growth and yields of tops and roots (8, 10, 14, 17) and decreased absorption nutrients (1, 8, 9, 13).

Experimental Methods

Surface soil from a Cherokee silt loam was used in this experiment. A 3 × 2 × 2 factorial experiment in a randoimsed complete block design with three replications was conducted in the green house. The details of treatments are :

Three factors (C, B, and A) :

1. C—Compaction at three levels

   c_0—(No compaction, 1·13 g./c.c. bulk density).

   c_1—(Medium compaction, 1·35 g./c.c. bulk density)

   c_2—(High compaction, 1·60 g./c.c. bulk density)

2. B—Fertilizer treatment at two levels

   b_0—(No fertilizer)

   b_1—(Fertilized at the rate equivalent to 87 lb P ; 166 lb K and 100 lb N per acre)

3. A—Aeration at two levels

   a_0—(No aeration)

   a_1—(aerated for four hours per day ; two hours in the morning and evening each)

The bottom five centimeters of soil in all the pots was so treated as to receive 40 ppm of rubidium chloride. This was necessary to make sure that there was a plentiful supply of rubidium in the soil.

Packing and Compaction of the Soil

One-gallon food cans, 15 cm in diameter and 17·5 cm. in height were used as experimental containers. The cans were provided with drainage vents at the bottom. Half the number of cans were provided with copper tubes through the drainage vents to facilitate aeration. A layer of sand (one centimeter thick) was spread over the bottom of the can and soil was packed over this sand in 2·5 cm. layers.

The required amounts of fertilizers were mixed with the soil to be packed into the fertilizer-treated cans. The required amount of soil for each compaction treatment was calculated from the volume of the soil column (12·5cm. × 15 cm.) and the bulk density required. Radioactive rubidium in the form of rubidium chloride was added to the bottom five centimeter column of the soil in each can. Rubidium chloride solution containing 7·029 mc. of Rb obtained from Oakridge National Laboratories was made upto 540 ml and five ml of this solution was added to each pot. This meant each can received 0·065 mc of activity at the start of the experiment. Over this five centimeter soil column, the rest of the soil for each can was packed in 2·5 cm layers. Each layer was tamped 25 times to get uniform packing. After packing each layer, the surface of each layer was scraped with a fork to prevent formation of layers in the soil column. Top four centimeters of the can was left vacant for watering purposes.

After packing the whole soil column, the top of the column around the wall of the can was sealed with sealing wax to prevent formation of cracks along the wall of the can.

Aeration and Moisture

Aeration was provided through the copper tubes in the drainage vents by the help of a pressure pump. Uniform aeration was ensured in all the cans by passing the air through a flask of water and by keeping the rate of bubbling constant in all the three compactions. All the cans were tested individually before the start of the experiment to ensure that air was passing through the whole soil column. Aeration was provided throughout the experiemntal period for four hours each day.

Moisture in the cans was maintained constant at 23·6 per cent throughout the experimental period by periodical weighing and addition of required water to make up the total weight. Sufficient care was taken to see that the soil never dried out, in order to prevent development of cracks which could permit extra air to enter the soil column. Ten seeds were planted in each can. The stand was thinned to four vigorously growing plants, at the end of one week.

Data collected and Analyses made

Root elongation into the radioactive layer was determined by a tracer technique. The plants were harvested at three stages, namely 20, 40 and 55 days after emergence. Shoot growth was determined after harvest on the basis of fresh and dry weight of the tops and nutrient uptake was obtained by analysing the tops for nitrogen, potassium, phosphorus and calcium.

The nitrogen was determined by Kjeldahl method. Dry plant material was prepared for chemical analysis by wet digestion with nitric and perchloric acid mixture. Phosphorus was determined colorimetrically using ammonium molybdate, hyrdrochloric acid and stannous chloride. Potassium and calcium were determined flame pbotometerically.

The radioactivity of the harvested plants was determined in the ground plant material with an end window type Geiger-Muller counter. Two tenths gram of material was taken for counting and the time of counting was varied with the sample, so as to get atleast 1000 counts. The counts per minute was calculated for each sample for comparison purposes. As the counting data were multiplicative in nature, logarithmic transformation of the data was made for statistical analysis. An assumption made in this case was that radioactivity in the plant was proportional to the root activity in the soil. The fresh and dry weights of the plants were recorded and chemical analysis made on the plant material. Nutrient uptake was calculated from yield and nutrient content of the plants. The data were analysed statistically.

Results and Discussion

Root growth : The radioactivity data are presented in table 1. The development of roots into the radioactive layer 7·5 cm below surface in every case decreased with increasing compaction. Aeration appeared to increase root development and fertilizers caused lower counts per minute except under the highest compaction level of the third stage where the activity was increased by fertilization.

The calculated radioactivity of the total dry matter is presented in table 2. Compaction reduced root elongation and the absorption of nutrients. Radioactivity was significantly lower in plants grown on more compact soils. Aeration significantly increased root activity; specially so in the high compaction treatments. Fertilization did not show any consistent increased in root activity except in the high compaction treatments. This discrepancy can be explained partly by the fact that Rubidium and potassium ions are competative in nature. An important

observation here was that fertility is very important when high compaction is present since non fertilized plants in high compaction treatments had very low activity. These observations are in agreement with those of Trouse and Humbert (18) and Wiersma (21).

Shoot growth : The oven dry weights of tops are presented in table 3. Significant differences were noticed due to compaction (C) and fertilization (B) in the first stage of growth and aeration showed no significant effect in the first stage. During the second stage aeration also showed significant effect on growth. In the third stage all the treatments and interaction were significant. This means that as the growth stage advances, the treatments and their interaction become more and more singnificant.

It is interesting to note that while the root activity was directly affected by compaction from a minimum of 1·35 g/cc., bulk densities somewhere between 1·35 and 1·60 g/cc. become critical to sunflower plants in this soil.

Nutrient uptake : The data of per cent nitrogen and the total nitrogen uptake by plants are presented in tables 4 and 5 respectively. As is seen from the tables the percent nitrogen decreased as the growth stage advanced. Lower percent nitrogen was recorded as the compaction level increased in the first stage. In the second and third stages, the nitrogen content was higher in the high compaction treatments. The percent nitrogen was higher in all the fertilized plant than in the non-fertilized plants. Aeration increased nitrogen content in high compaction treatments.

The total nitrogen uptake decreased with compaction in all three stages. Aeration increased the total uptake of nitrogen. All the three main treatments showed significant differences in nitrogen uptake in all three stages. None of the interactions were significant in the first stage, indicating that all the main treatments were acting independently in the early stage of growth.

The data of percent phosphorus in plants and the total uptake of phosphorus are presented in table 6 and 7. The phosphorus content decreased with compaction, in the first and second stages whereas in the third stage the percent phosphorus was higher in the high compaction treatments. Phosphorus content decreased with aeration with unfertilized but increased when fertilized. The results indicated that the phosphorus content was low under compacted conditions during the active growth stages ; but during the reproductive stage the P content increased due to compaction. The total uptake of phosphorus was in general low in high compaction treatments. Fertilized plants absorbed in general less total phosphorus than others. There was an overall increase in uptake of phosphorus due to aeration. All the main treatments and interactions were significant in the second and third stages, indicating that as the growth advanced, the treatments depended upon each other for their action as phosphorus uptake.

The data of percent potassium in plants and the total uptake of potassium are presented in tables 8 and 9 respectively. Potassium content was low in high compaction treatments in the first stage. In the second and third stages more potassium was found in high compaction treatments when the plants were fertilized and less when the plants were non-fertilized. Aeration did not produce higher percentage of potassium in plants. Fertilized plants contained higher percentage of potassium.

The total potassium uptake decreased with compaction. Aeration had not given consistent increase in potassium uptake.

TABLE 1

Radioactivity (counts per minute)

(0·2 g. material)

	First stage			Second stage			Third stage		
	c_0	c_1	c_2	c_0	c_1	c_2	c_0	c_1	c_2
b_0a_0	1998	1079	11	2435	2019	25	776	451	5
b_1a_0	1335	290	19	1085	502	34	252	139	30
b_0a_1	2588	1796	49	3705	1949	66	998	462	13
b_1a_1	1384	393	25	1490	762	43	406	151	34

TABLE 2

Radioactivity (log. activity)

(Average of three replications : Total activity in four plants)

	First stage			Second stage			Third stage		
	c_0	c_1	c_2	c_0	c_1	c_2	c_0	c_1	c_2
b_0a_0	4·33	4·06	2·00	4·95	4·87	2·70	4·79	4·52	2·33
b_1a_0	4·42	3·73	2·50	4·96	4·61	3·29	4·60	4·26	3·70
b_0a_1	4·52	4·29	2·71	5·19	4·90	3·22	4·23	4·52	3·15
b_1a_1	4·46	3·86	2·63	5·10	4·79	3·45	4·80	4·34	3·77
Mean	4·43	3·99	2·46	5·05	4·79	3·17	4·61	4·41	3·24

TABLE 3

Oven dry weights of tops (grams)

(Average of three replications : Weights of four plants)

	First stage			Second stage			Third stage		
	c_1	c_1	c_2	c_0	c_1	c_2	c_0	c_1	c_2
b_0a_0	2·17	2·13	1·83	7·27	7·30	4·00	15·87	14·47	8·50
b_1a_0	3·93	3·77	3·33	16·93	16·47	11·67	27·70	26·23	23·87
b_0a_1	2·57	2·17	2·13	8·33	8·13	5·10	15·73	14·27	11·10
b_1a_0	4·17	3·70	3·40	16·83	16·13	13·30	30·80	29·00	26·67
Mean	3·21	2·94	2·67	12·34	12·01	8·52	22·53	20·99	17·54

TABLE 4

Percent Nitrogen in plants

	First stage			Second stage			Third stage		
	c_0	c_1	c_2	c_0	c_1	c_2	c_0	c_1	c_2
b_0a_0	3·05	3·04	2·24	0·93	0·90	1·02	0·59	0·64	6·68
b_1a_0	3·36	3·10	2·61	1·17	1·18	1·30	0·66	0·66	0·74
b_0a_1	2·87	3·17	2·28	0·73	0·89	1·22	0·63	0·59	0·66
b_1a_1	3·21	3·22	3·12	1·19	0·93	1·41	0·66	0·67	0·87

TABLE 5

Nitrogen Uptake (milligrams)

(Average of three replications : Total uptake by four plants)

	First stage			Second stage			Third stage		
	c_0	c_1	c_2	c_0	c_1	c_2	c_0	c_1	c_2
b_0a_0	66·20	64·70	41·19	67·96	67·19	41·09	93·67	92·98	57·88
b_1a_0	131·96	116·35	86·99	197·17	194·42	151·60	181·82	172·15	177·27
b_0a_1	73·67	68·76	48·66	60·83	72·89	61·77	98·55	84·25	73·38
b_1a_1	133·93	119·04	106·18	199·31	149·32	187·40	204·01	193·18	224·11
Mean	101·44	92·21	70·76	131·32	120·96	110·47	144·51	135·64	133·16

TABLE 6

Percent Phosphorus in plants

	First stage			Second stage			Third stage		
	c_0	c_1	c_2	c_0	c_1	c_2	c_0	c_1	c_2
b_0a_0	0·207	0·187	0·156	0·090	0·118	0·087	0·074	0·061	0·099
b_1a_0	0·271	0·261	0·164	0·130	0·148	0·103	0·088	0·108	0·075
b_0a_1	0·165	0·164	0·140	0·093	0·098	0·088	0·074	0·061	0·095
b_1a_1	0·233	0·262	0·197	0·164	0·152	0·126	0 094	0·127	0·096

TABLE 7

Phosphorus Uptake (milligrams)

(Average of three replications : Uptake by four plants)

	First stage			Second stage			Third stage		
	c_0	c_1	c_2	c_0	c_1	c_2	c_0	c_1	c_2
b_0a_0	4·48	3·98	2·86	6·58	8·62	3·49	11·76	8·57	8·41
b_1a_0	10·65	9·83	5·47	21 92	24·23	11·94	24·34	28·31	17·81
b_0a_1	4·21	3·55	3·00	7·78	7·96	4·46	11·98	8·75	10·52
b_1a_1	9·69	9·68	6 68	28·29	24·54	16·81	28·88	37·45	25·60
Mean	7·26	6·76	4·50	16·14	16·34	9·18	19·24	20·77	15·59

TABLE 8

Percent Potassium

	First stage			Second stage			Third stage		
	c_0	c_1	c_2	c_0	c_1	c_2	c_0	c_1	c_2
b_0a_0	1·33	1·33	0·97	0·73	0·73	0·85	0·58	0·67	0·85
b_1a_0	2·33	2·03	1·53	1·05	1·22	0·67	0·78	0·72	0·57
b_0a_1	1·30	1·45	0·90	0·75	0·63	0·67	0·58	0·65	0·83
b_1a_1	2·63	2·07	1·50	1·03	0·93	0·72	0·80	0·82	0·77

TABLE 9

Potassium Uptake (milligrams)

(Average of three replications : Uptake by four plants)

	First stage			Second stage			Third stage		
	c_0	c_1	c_2	c_0	c_1	c_2	c_0	c_1	c_2
b_0a_0	39·57	28·40	17·83	53·75	53·50	34·30	92·65	98·43	72 25
b_1a_0	91·80	76·27	51·07	177·32	222·60	79·37	216·98	198·05	135·37
b_0a_1	33·43	31·80	19·13	64·53	46·00	36·13	88·25	92·72	92·63
b_1a_1	109·70	76·47	51·20	173·83	150·33	98·57	246·07	236·75	204·55
Mean	68·63	53·24	34·81	117·36	118·11	44·59	160·99	156·49	126·20

TABLE 10

Percent calcium in plants

	First stage			Second stage			Third stage		
	c_0	c_1	c_2	c_0	c_1	c_2	c_0	c_1	c_2
b_0a_0	2·95	3·00	2·65	1·93	1·63	3·30	1·90	1·45	2·46
b_1a_0	2·64	2·64	2·84	1·90	1·86	2·21	1·49	1·41	1·82
b_0a_1	3·37	3·20	3·20	1·96	1·81	2·67	1·65	1·69	1·80
b_1a_1	2·48	2·43	2·97	1·80	1·73	2·33	1·89	1·43	1·91

TABLE 11

Calcium Uptake (milligrams)

(Average of three replications : Uptake by four plants)

	First stage			Second stage			Third stage		
	c_0	c_1	c_2	c_0	c_1	c_2	c_0	c_1	c_2
b_0a_0	63·84	64·01	48·61	140·49	118·75	132·33	304·55	209·75	208·94
b_1a_0	103·92	99·84	94·69	320·15	304·93	257·44	413·32	370·78	435·38
b_0a_1	86·43	69·32	67·75	163·20	147·47	134·11	259·79	241 95	199·53
b_1a_1	103·43	91·23	101·92	302·82	279·36	313·20	580·28	415·69	508·97
Mean	89·41	81·10	78·24	231·67	212·63	209·47	389·49	309·54	338·21

The percent calcium and the total uptake of calcium by plants are presented in tables No. 10 and 11 respectively. In the first stage the percent calcium increased with compaction when no fertilised and increased with fertilization. In the second and third stages, the percent calcium decreased from low to medium compaction and again increased in high compaction treatment. Aeration did not have any consistent effect on percent calcium in plants.

The total uptake of calcium was lower in all high compaction treatments than in others. Aeration had no consistent effect on total calcium uptake. The total uptake of calcium was higher in all the fertilized treatments than in unfertilized ones.

Summary

A factorial pot experiment in a randomized complete block design with three replications was conducted in the greenhouse with Cherokee silt loam soil, to determine the effect of soil compaction in combination with aeration and feritliza-tion, on root activity, top growth and nutrient uptake of sunflower plants.

Root activity was determined by a tracer technique using radioactive rubidium (Rb^{86}) ; top growth was obtained by recording the fresh and dry weights of tops ; and nutrient uptake was determined by analyzing the plant material for nitrogen, phosphorus, potassium and calcium. All the data were collected at three stages of growth, namely 20, 40 and 55 days growth after emergence. The data were analyzed statistically.

The root activity as measured by radioactivity in the plant decreased with compaction of the soil. Aeration significantly increased the root activity in all three stages. The increase in root activity due to aeration was more pronounced in all high compaction treatments. Fertilization caused higher root activity only in the high compaction treatments, in the second and third stages. The three factor interactions (A × B × C) in all three stages were significant. It must be concluded that both mechanical impedance and poor aeration contribute to poor root activity in compacted soils, though it was not possible to determine the magnitude of the effect of each of the two factors.

The top growth was severely affected by high compaction (1·60g./c.c bulk density). Medium compaction had little effect on top growth of plants. Aeration increased the top growth in all three stages ; but the increase was statistically significant only in the second and third stages of growth. The increase was more pronounced in the high compaction treatments. Thus, it appears that forced aeration can overcome some but not all the bad effects of soil compaction. Fertilization more than compensated for the bad effects of high compaction.

The percent nitrogen increased with compaction in the second and third stages ; decreased with compaction in the first stage ; decreased as the growth stage advanced and increased with fertilization. The percent phosphorus in plants increased with fertilization ; decreased with compaction in the first and second stages and increased in the high compaction treatments in the third stage ; and increased with aeration when plants were fertilized, but decreased when the plants were not fertilized. The percent potassium in plants was low in high compaction treatments in the first stage. In the second and third stages, potassium content of plants was greater in high compaction treatments when plants were not fertilized and less when fertilized. In general, all fertilized plants contained higher percentage of potassium. Aeration did not produce consistent results with respect to potassium content of plants. The percent calcium in the first stage, decreased with compaction when not fertilized and increased when fertilized. In the second and third stages, the percent calcium decreased from low to medium compaction and again increased in high compaction treatmeats. Aeration had no consistent effect on percent calcium in plants. Fertilized plants in general, had lower percentages calcium than non-fertilized plants.

In general, severe compaction reduced the total uptake of all the nutrients studied, by sunflowers. Forced aeration increased the uptake of nitrogen, and phosphorus, especially on the high compaction treatments. The effect of acration on potassium and calcium was quite variable. Fertilizer application increased the uptake of fertilizer elements nitrogen, phosphorus and potassium. Even calcium uptake was increased by fertilization. However, the latter must have resulted from an overall growth increase, because the percent calcium of fertilized sunflowers was lower than unfertilized plants.

Acknowledgement

Thanks are due to Dr. J. A. Hobbs, Professor of Agronomy, Kansas State University, U. S. A. for his keen interest and guidance in the study.

References

1. Arnon, D. I. and Hoagland, D. R. Crop production in artificial culture solutions and in soils with special reference to factors influencing yields and absorption of inorganic nutrients. *Soil Sci.* **50** : 463, 1940.
2. Baver, L. D. Soil physics. *John Wiley and Sons Inc. New York,* 3rd Ed. 1956.
3. Baver, L. D. and Farnsworth, R. B. Soil structure effects in the growth of sugar beets. *Soil Sci. Amer. Proc.* (1940). **5** : 45–48, 1941.
4. Beatrand, A. R. and Kohnke, H. Subsoil conditions and their effects on oxygen supply and the growth of corn roots. *Soil Sci. Soc. Amer. Proc.* **21** : 135–140, 1957.
5. Brind, W. D. Some German and Austrian work on soil compaction and fertility. *Soils and Ferti.* **15** : 227-230, 1952.
6. Crossby, D. I. The effect of a compact subsoil horizon on root penetration. *Jour. Forestry.* **38** : 794–796, 1940.
7. De Roo, H. C. Root Development in coarse textured soils as related to tillage practices and soil compaction. *Trans. 7th Int. Cong. Soil Sci. Madison, Wis.* **Vol. I**, 622-628, 1960.
8. Flocker, W. J., Vomooil, J. A. and Howard, F. D. Some growth responses of tomatoes to soil compaction. *Soil Sci. Soc. Amer. Proc.* **23** : 188–191, 1959.
9. Harris, D. C. and Van Bavel, C. H. M. Nutrient uptake and chemical composition of tobacco plants as affected by the composition of root atmosphere. *Agron. Jour.* **49** : 176-181, 1957.
10. Lawton, K. The influence of soil aeration on the growth and absorption of nutrients by corn plants. *Soil Sci. Soc. Amer. Proc.* **20** : (1945) **10** : 263–268, 1946.
11. Lutz, J. F. Mechanical impedence and plant growth. *In* Shaw, B. T. Editor, Soil Physical Conditions and Plant Growth. Agronomy Monograph **Vol. 2**, 43–72. *Academic Press Inc. New York,* 1952.
12. Meredith, H. L. and Pattrick, W. H. Jr. Effects of soil compaction and physical properties of three soils in Louisiana. *Agron. Jour.* **53** : 163–167, 1961.
13. Popkowitz, L. P. and Shive, J. W. The importance of oxygen in nutrient substrate for plants—Ion absorption. *Soil Sci.* **57** : 143–154, 1944.
14. Phillips, R. E. and Kirkham, Don. Soil compaction in the field and corn growth. *Agron. Jour.* **54** : 29–34, 1962.
15. Raney, W. A., Edminister, T. W. and Allaway, W. H. Current status of research in compaction. *Soil Sci. Soc. Amer. Proc.* **19** : 423-428, 1955.
16. Smith, F. W. and Cook, R. L. The effect of soil aeration, moisture and oxidation and growth of sugar beets following corn and legumes in pot culture. *Soil Sci. Soc. Amer. Proc.* (1946) **11** : 402–406, 1947.

17. Swanson, C. L. W. and Jacobson, H. G. N. Effects of soil hardness and compaction on corn growth. *Soil Sci. Soc. Amer. Proc.* **20** : 161-167, 1956.

18. Trouse, A. C. Jr. and Humbert, R. P. Some effects of soil compaction on the development of sugarcane roots. *Soil Sci.* **91** : 208-217, 1961.

19. Veihmayer, F. J. and Hendrickson, A. H. Soil density as a factor in determining the permanent wilting percentage. *Soil Sci.* **62** : 451-456, 1946.

20. Veihmayer, F. J. and Hendrickson, A. H. Soil density and root penetration. *Soil Sci.* **65** : 487-493, 1948.

21. Wiersma, D. The soil environment and root development. *In* Advances in Agronomy **Vol. XI**, 43-51. *Academic Press Inc. New York*, 1959.

22. Winters, Eric and Simonson Roy, W. The subsoil. *In* Advances in Agronomy **Vol. III**, 1-92. *Academic Press Inc. New York*, 1951.

Proc. Nat. Acad. Sci., India, 38 (A), I & II, 1968

Phosphate leaching from soils

By

N. R. DHAR *and* M. K. FOTEDAR

Sheila Dhar Institute of Soil Science, University of Allahabad, Allahabad

The phosphate status of Indian soils is continually decreasing. Major part of this decrease is due to its removal by plants and a part, which is lost, due to washing away. Since phosphates are indispensable for proper plant growth, a systematic investigation on the phosphate loss due to washing away has been undertaken. The aim is to have a quantitative idea about this loss under different conditions prevailing in India.

A large number of workers in Europe have studied this problem. Ulbricht (1) using displacement technique obtained amounts of P_2O_5 in soil solutions ranging from 1 p.p.m. to 16 p.p.m. in poor and good soils respectively. Way (2) obtained small amounts of phosphate in drainage waters. Voelcker (3) working at Rothamsted obtained 0·6 and 1·54 p.p.m. of P_2O_5 in the drainage waters of unmanured and manured plots respectively. Hall (4) pointed out that Rothamsted surface soils loss 1 kgm. of P_2O_5 per acre by leaching. Lyon and Buckman (5) have reported a loss of 4 lbs. of P_2O_5 in drainage waters per acre. MacIntire and Sterges (6) have reported a loss of 0·3 lb. of P from a soil having a pH between 6·7 to 7·4 receiving 50·8 inches of rain annually. Robinson and Jones (7) have reported marked losses of phosphates from red soils of Wales where the rainfall is very high. Scarseth and Chandler (8) have reported that loss of phosphate may be serious where there is much run-off water. The organic matter content and the fertilisation practices also effect the loss of phosphates from soils to a great extent. Gaarder (9) found that humid soils of high humus content lose more phosphate.

No systematic study has been made so far regarding the losses of phosphates from Indian soils. Dhar and Misra (10) have worked with some U. P. soils. They reported a loss of 6·2 and 0·25 lb per acre from rich and poor soils respectively. The present investigation has, therefore, been undertaken in order to study the relative loss of phosphate from Kashmir soils. Two types of soils were taken for the experiments. The first type (A-soil) was rich in organic matter and phosphate while the second type (P-soil) was poor in both these constituents.

Experimental

The soils were air-dried and ground to pass through a 100-mesh sieve. Known weights of these samples were shaken with varying amounts of distilled water for 2 hours At the end of this time, the contents were kept at a 'Control' temperature of 30°C for 24 hours and then filtered. The soils were again transferred and the required volume was made up and the contents shaken as before. In this way a number of washings were taken with the soil : water ratios of 1 : 2, 1 : 5, 1 : 10, 1 : 25, 1 : 50 and 1 : 100 in order to imitate the leaching of soil in nature under different amounts of rainfall. The soils were then analysed for their residual P_2O_5 content and the amount of P_2O_5 lost in all the washings calculated in lbs per acre assuming the weight of 1 acre of soil upto 6 inches depth to be 2 million lbs.

In other set of similar experiments, various extracts from washings were analysed for their P_2O_5 contents and the P_2O_5 was determined colorimeterically using hydroquinone as the reducing agent—Arrhenius (11).

Results

TABLE 1

P_2O_5 and organic matter content of the soils

Soil Type	Total P_2O_5 %	Available P_2O_5 %	Organic matter %	pH
A – soil	0·209	0·0585	2·58	8·5
P – soil	0·113	0·0200	1·45	5·2

TABLE 2

Loss of P_2O_5 in lbs per acre at various soil-water ratios

	SOIL - WATER RATIOS					
A – *soil*	1 : 2	1 : 5	1 : 10	1 : 25	1 : 50	1 : 100
Total loss of P_2O_5	40·0	58·0	166·0	504·0	948·0	1640·0
Loss per washing	2·22	3·32	3·32	10·08	18·96	32·0
P – *soil*						
Total loss of P_2O_5	9·6	–	20·04	30·0	–	–
Loss per washing	0·21	–	0·501	0·66	–	–

TABLE 3

Amount of P_2O_5 released in various extracts of A – soil in lbs per acre

	SOIL-WATER RATIOS		
No. of extract	1 : 10	1 : 25	1 : 50
First	48·04	96·0	112·2
Fifth	36·03	68·3	84·5
Tenth	14·2	42·4	69·0
Fifteenth	10·2	36·0	54·0

TABLE 4

Amount of P_2O_5 released in various extracts of P – soil in lbs per acre

	SOIL-WATER RATIOS		
No. of extract	1 : 10	1 : 25	1 : 50
First	2·70	27·0	43·0
Fifth	–	20·0	30·2
Tenth	–	15·6	23·6
Fifteenth	–	13·5	20·8

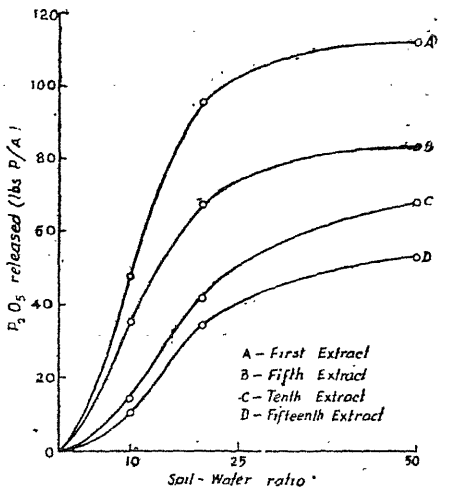


Fig 1 – Amount of P_2O_5 released in various extracts of A-Soil at various soil-water ratios

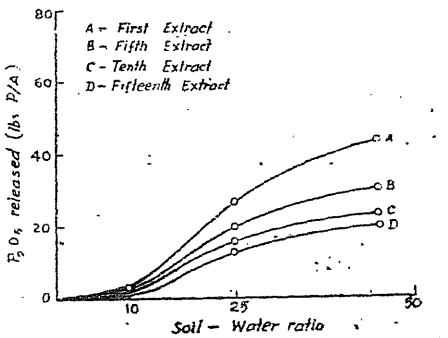


Fig. 2 – Amount of P_2O_5 released in various extracts of P-Soil at various soil-water ratios

Discussion

From a close study of the results in Table No. 2, it is found that a phosphate-rich soil loses more phosphate per washing than a soil poor in phosphate. The amount of phospnate lost at higher soil-water ratios in the case of phosphate-rich soil is marked in comparison to a phosphate-poor soil. A-soil is found to lose more phosphate than P-soil. It can be calculated from the results in Table No. 2 that at a place getting an annual rainfall of 25 inches, about 40 lbs of P_2O_5 are lost per acre in 18 years (soil-water ratio 1 : 2) from a soil rich in phosphate whilst only 9·6 lbs of P_2O_5 are lost per acre from a phosphate-poor soil. If this loss at various soil : water ratios is calculated as a percentage of the total P_2O_5, it is found to vary from 0·85 to 4·5% in the case of A-soil and from 0·5 to 1·5% approx. in the case of P-soil. Jensen (12) reported that water extracts of decomposing organic matter are much more effective than water in dissolving phosphates from soils. This is accounted for by the liberation of organic acids in the soil

due to the slow oxidation of organic matter. These organic acids enhance the solubility of the various phosphates present in the soil. Thus, A-soil rich in organic matter loses more phosphate than the P soil poor in organic matter. It can, therefore, be concluded that the depletion of phosphate is more in the case of phosphate and organic matter-rich soils in comparison to soils poor in both these constituents.

From Figures 1 and 2 it is clear that the rate of release of P_2O_5 shows a rapid decrease for the first few extracts followed by a slower decrease and finally a near leveling off. This leveling took place by the 12th extract and the rate remained approximately constant through the subsequent extracts. Fried *et al* (13) obtained similar results and reported that the rate of release of P_2O_5 remains nearly constant after the 10th extract. The rate of release in the case of A-soil is more in comparison to P-soil showing thereby that the original P_2O_5 content also influences the rate of release. Thus, soils with the higher P_2O_5 content are apt to lose more phosphate than soils with low P_2O_5 content. It is also seen that the rate of release is enhanced to a great extent at higher soil : water ratios. Thus, at places receiving larger rainfalls, the loss due to leaching is marked.

Summary

The amount of phosphate present in the water extract of soils depends mainly upon their original phosphate status, organic matter content and the soil-water ratio. It has been observed that a soil rich in phosphate and organic matter loses a great deal of phosphate in comparison to a soil poor in these constituents. The loss is markedly increased with increasing soil-water ratios.

References

1. Hilgard, E. W. Soils, *Reinhold Pub. Corp., New York*, 330, 1906.
2. Way, J. T. *J. Royal Agric. Soc.*, **17** : 123, 1856.
3. Voelcker, J. A. *Trans. Chem. Soc.*, **24** : 276-297, 1871.
4. Hall, A. D. Book of Rothamsted Experiments, 238, 1903.
5. Lyon, T. L. and Buckman, H. O. The nature and properties of soils, *Macmillan & Co., New York*, IVth ed., 1943.
6. MacIntire, W. H. and Sterges, A. J. *Soil Science*, **74** : 233-274, 1952.
7. Robinson, G. W. and Jones, J. O. *J. Agric. Sci.*, **17** : 94, 1927.
8. Scarseth, G. D. and Chandler, W. W. *J. Amer. Soc. Agron.*, **30** : 361, 1938.
9. Gaarder, T. *Vestlandets Forstlige Forsotation Meddel*, **14** : 1930.
10. Dhar, N. R. and Misra, S. G. *Pro. Nat. Acad. Sci., India*, **25A** : 420 432, 1956.
11. Arrhenius, O. Ethnos, 2-4, 1963.
12. Jensen, C. A. *J. Agri. Research*, **9** : 253-268, 1917.
13. Fried, M. *et al. Soil Science*, **84** : 427-437, 1957.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968

Loss of organic carbon from soils by nitrogenous substances

By

N. R. DHAR *and* A. K. RISHI

Sheila Dhar Institute of Soil Science, University of Allahabad, Allahabad

Though synthetic nitrogen helps to increase the crop growth but its continuous use is detrimental to the maintenance of land fertility. Russell[1] has shown that the persistent use of fertilizers leads to the deterioration of soil structure and soil tilth. Application of sodium nitrate reduces permeability[2,3]. Use of ammonium sulphate may break down the soil structure.[4]

Mineral fertilizers when added to soil create acidity which greatly hinders the beneficial soil processes. Barnette *et al*[5] and Pierre[6] in more recent years have observed an increase in the hydrogen ion concentration in the soil solution when ammonium sulphate was added to soils. Loss of exchangeable calcium was established by Wheeler[7] and Voelcker[8]. Lime requirement of soils receiving artificial fertilizers was extensively worked out by White and Holben[9] and Allison and Cook[10]. 143 lbs of calcium carbonate are required to neutralise the acidity produced in soil by 100 lbs of ammonium sulphate[10].

The researches of Russell and Richards[11] and others show that nitrogen in the gaseous state is lost from the soils when the conditions are favourable for oxidation. Nearly 70% of the added nitrogen is reported to have been lost when wheat plots in Rothamsted (England) received 14 tons of farmyard manure containing 200 lbs. of nitrogen per acre. Dhar and Pant[12] have reported considerable losses of nitrogen in soils and oxide surfaces on the decomposition of nitrogenous substances in the complete absence of micro-organisms under aerobic conditions. Lohnis and Fred[13] have reported 7·8–46·1% recovery of nitrogen from the field experiments lasting four years.

In addition to the fact that huge losses of nitrogen are suffered when nitrogenous substances are added to soils, it has been widely reported that artificial nitrogenous fertilizers have a corrosive effect on the soil humus. Saloman and Smith[14] studied the chemical characteristics of soils after 53 years of fertilization with sodium nitrate and ammoniun sulphate and found among other things a downward movement of organic matter. Enhanced loss of carbon from straw due to oxidation by the addition of ammonium sulphate was reported by Simon and Barbier[15]. Lykov[16] after 48 years of experimentation observed that the soil had lost 28% of its humus when NPK was applied and 18% when dung was applied.

The aim of present investigations has been to study the oxidation of soil humus carbon by different inorganic and organic nitrogenous substances.

Experimental and Discussion

From a large number of experiments carried on in this laboratory we have conclusively established among other things that humus carbon suffers a great loss when nitrogenous substances are incorporated into soils. The rate of carbon oxidation is much enhanced when 0·2% N as ammonium sulphate, ammonium nitrate, ammonium phosphate and ammonium persulphate is added to Allahabad loam containing 0·9458% carbon, 0·0775% nitrogen, 0·24% P_2O_5 and 1·86% CaO and having a pH of 7·45. The results are recorded in Table 1.

TABLE 1

Oxidation of carbon after 300 days in 200 gms. of soil

Treatment 0·2% N	Carbon oxidised (gm) Exposed	Covered	% carbon oxidised Exposed	Covered	pH Exposed	Covered
Soil alone	0·2877	0·2045	15·2	10·8	7·25	7·30
Soil + ammonium sulphate	0·3452	0·2425	18·2	12·8	4·95	6·00
Soil + ammonium nitrate	0·3708	0·2662	19·6	14·1	5·50	6·45
Soil + ammonium phosphate	0·3959	0·2910	20·9	15·4	6·80	7·00
Soil + ammonium persulphate	0·4566	0·3472	24·1	18·4	6·85	7·05

It is evident from the foregoing observations that percentage oxidation of organic carbon after 300 days is 15·2 and 10·8 in exposed and covered sets respectively in soil without any amendment. The oxidation of humus carbon is increased to 24·1 % and 18·4 % in exposed and covered sets respectively when 0·2 % N as ammonium persulphate is added to soil. The loss of humus carbon with different nitrogenous substances is in the following order :

Ammonium persulphate > Ammonium phosphate > Ammonium nitrate > Ammonium sulphate.

Curiously enough pH of the system is in the same descending order.

It is well known that ammonium salts are oxidised to nitrate in soil which on its part is responsible for enhancing the oxidation of humus carbon.

Greater oxidation in the system containing ammonium phosphate than the sets having ammonium nitrate or ammonium sulphate may be due to the slightly alkaline nature of ammonium phosphate.

When the effect of ammonium persulphate is considered we have to bear in mind that ammonium persulphate undergoes the following change in aqueous solution :

$$4(NH_4)_2S_2O_8 + 3H_2O = 7(NH_4)\,HSO_4 + HNO_3 + H_2SO_4$$

As ammoninm persulphate as well as the nitric acid produced are strong oxidising agents, the slow oxidation of organic matter is enhanced due to the addition of ammonium persulphate.

Experiments conducted with organic nitrogenous substances also showed an increase in the loss of humus carbon. The results are recorded in Table 2.

TABLE 2

Oxidation of carbon after 300 *days in* 200 *gms. of soil*

Treatment 0·2 % N	Carbon introduced due to nitrogenous Substances (gm)	Carbon oxidised (gm)		Loss of humus carbon due to nitrogenous substances (gm)	
		Exposed	Covered	Exposed	Covered
Soil Alone	–	0·2877	0·2045	–	–
Soil + Urea	0·1714	0·5992	0·4711	0·1401	0·0952
Soil + Uric acid	0·4286	0·7878	0·6569	0·0715	0·0238
Soil + Hippuric acid	3·0864	3·4634	3·3173	0·0893	0·0264
Soil + Glycine	0·6858	1·0952	0 9560	0·1217	0·0657
Soil + Creatine	0·4572	0·8493	0·6959	0·1044	0·0342
Soil + Gelatine	1·0498	1·4511	1·2918	0·1136	0·0375
Soil + Mustard oil cake	3·6306	4·0749	3·9357	0·1566	0·1006

The foregoing results indicate that greater the amount of carbon introduced at the initial stage by the organic nitrogenous substance, the greater is the velocity and the amount of oxidation of carbonaceous matter; this is in general agreement with the law of mass action. In all cases oxidation of carbon is greater in the systems exposed to light than those kept covered with black cloth. Moreover, the comparison of the loss of humus resulting by the addition of organic nitrogenous substances to Allahabad soil shows the following decreasing order :

Mustard oil cake > Urea > Glycine > Gelatine > Creatine > Hippuric acid > Uric acid.

Greater loss of humus carbon by the application of mustard oil cake is due to the fact that pH is raised from 7·45 to 8·55 and 8·45 after 200 days in the sets exposed to light and kept covered respectively.

Dhar and Rishi[17] have observed that with all these nitrogenous substances nitrification is quicker than ammonification. Thus the nitrate produced enhances the oxidation of humus carbon.

From the foregoing results it is quite clear that if the use of artificial nitrogenous fertilizers continues at the present rate the soils shall, in due course of time, get impoverished in humus and thus pose a great threat to agriculture and life on this planet. Hence, in order to increase the nitrogen and humus status of soils and, thereby, the fertility, the addition of nitrogenous fertilizers should always be supplemented by a mixture of organic matter and phosphate. If the phosphate source be basic slag the acidity caused by mineral fertilizers can be counteracted.

Summary

The influence of different nitrogenous fertilizers like ammonium sulphate, ammonium nitrate, urea etc. on the oxidation of carbon in Allahabad loam was studied.

Observations indicate that nitrogenous substances appreciably enhance the oxidation of carbon and, thereby, result in the loss of soil humus.

References

1. Russell, E. J. Soil conditions and plant growth, VIII ed., 409, 1950.
2. Aldrich, D. G., Parker, E. R. and Chapman, H. D. *Soil Sci.*, **59** : 229, 1945.
3. Fireman, M. and Wilcox, L. V. *Calif. citrograph.*, **29** : 196, 1944.
4. Fox, R. L., Olson, R. A. and Mazurak, A. P. *Agronomy Journal*, **44** : 509, 1952.
5. Barnette, A. M. and Hester, J. B. *Soil Sci.* **30** : 431, 1930.
6. Pierre, W. H. *Ind. Eng. Chem.*, **23** : 1440, 1931.
7. Russell, E. J. Soil conditions and plant growth, VIII ed., 118-120, 1950.
8. *Ibid*, p. 120.
9. White, J. W. and Holben, F. J. *Penn. Agr. Exp. Sta. Bull.* , 195, 1925.
10. Allison, F. E., and Cook, R. C. *Soil Sci.*, **3** : 507, 1917.
11. Russell, E. J. and Richards, H. *Jour. Agr. Res.* **8** : 405, 1917.
12. Dhar, N. R. and Pant, N. N. *Nature*, 1942.
13. Lohnis, F. and Fred, E. B. Text book of Agricultural Bacteriology, 224, 1923.
14. Salomon, M. and Smith, J. B. *Soil Sci. Soc. Am. Proc.*, **12** : 296, 1948.
15. Simon, Mme. G. and Barbier, G. *Pro. L'Acad'mie D'Agriculture de France*, **14** : 1206-9, 1963.
16. Lykov, A. M. *Dokl. S Kh. Akad. Timiryazeva*, **71** : 25-31, 1961.
17. Rishi, A. K. *D.Phil Thesis. University of Allahabad*, 1964.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968

Reclamation of Alkali soil (I)

By

N. R. DHAR *and* A. K. RISHI

Sheila Dhar Institute of Soil Science, University of Allahabad, Allahabad, (India)

Introduction

India, with a vast population of 476 million and three-fourths of it dependant on agriculture, leads the sufferring nations of the world. At present the country is on the verge of starvation, as is evident from the food intake of Indian citizens which is hardly half of the average requirement to keep body and soul together.

Such a crisis can be averted by increasing the food production. Hence it is imperative to improve the land already under cultivation by improved methods of agriculture. Moreover, equal emphasis has to be laid to bring unculturable wastelands under plough It is known that nearly 170 million acres of land, which includes arid land, land unfit by erosion and alkaline land is lying waste, in this country (1). In addition to the existing alkaline lands, Raychaudhury and Dutta-Biswas (2) have estimated that 5000 sq. miles of alkali lands have been formed due to the introduction of irrigation through canal system to the arid and semi-arid regions of Punjab, U. P., and Bombay-Deccan.

These soils, according to many workers can only be effectively reclaimed by changing their chemical nature by transforming these sodium soils into calcium soils. Various methods of reclamation by the application of amendments like gypsum (3, 4,) sulphur and sulphuric acid (5,6) etc. etc. have been tried in Holland, Egypt, Russia, Hungary and the U. S. A. with a fair amount of success. Reclamation of alkali land by merely leaching out of the salts by flooding with water has also been reported (7, 8, 9). But these methods do not appear to bring about a permanent reclamation (4) and, besides this, they are too expensive for a poor country like ours.

According to Singh (10) algae can be used in the reclamation of *Usar* lands. This claim needs further substantiation.

Unlike the soils of temperate countries, the alkali soils of India are generally deficient in their organic matter and nitrogen content. This significant fact must be taken into consideration while studying the problem of alkali land reclamation in India.

Dhar was a pioneer in discovering the use of organic matter and phosphates in the reclamation of alkali lands. Dhar and coworkers (11) have carried out numerous experiments and some of them (12, 12*a*) at Soraon (Allahabad) and Bhupalsagar (Rajasthan) on the reclamation of alkali soil and obtained very significant yield of paddy and barley crops with molasses, pressmued and other organic materials along with calcium phosphates in the form of bone meal and slags etc. Beneficial effect of organic matter on the reclamation of alkali soils have also been reported from Russia (13) and Belgium also (14).

In the present investigations the authors have made an endeavour to explore the possibilities of reclaiming alkali soils by waste materials like coal, water hyacinth and KANS (Sacchrum spontaneum) in conjunction with Tata basic slag and Trichinopoly rock phosphate.

Methods and Materials

The field experiments were carried on at Babuganj, 6 miles from Phulpur (Allahabad) Rly. Station. The area which we selected for our field experiments was lying uncultivated due to alkalinity. The field was ploughed and the amendments were mixed on 15th June, 1962. Coal and KANS (Sacchrum spontaneum) were ploughed in dry condition and water hyacinth was ploughed in green condition. Wherever required Tata basic slag and Trichinopoly rock phosphate were incorporated. Soil samples before and 60 days after the incorporation were analysed. The plots were kept moistened before the rains started. Gram was sown on 15th December, 1962 after preparing the plots. Gram was harvested on 25th March, 1963. After the harvest of gram crop, soil samples were collected from each plot and were analysed. The plots were again prepared and paddy (N-22) was transplanted in lines on 1st August, 1963. The distance from plant to plant and row to row was kept at 9 inches. Paddy was harvested on 26th October, 1963. After the harvest of the paddy crop, soil samples were collected from each plot and were analysed. The plots were again prepared and wheat (N.P. 165) was sown on 15th November, 1963. Wheat crop was harvested on 2nd April, 1964. Composite soil samples were again collected from different plots and were analysed. Tube well water was used for irrigation purposes.

Design of the experiments	Randomised block layout
Number of treatments	13
Number of replications	4
Number of plots	52
Area of the plot	1/60th of an acre
Size of the plot	33′ × 22′
Rate of amendments	5 tons/acre
Phosphates (Tata basic slag and Trichinopoly rock phosphate)	50 lbs P_2O_5/acre
N,P,K in the form of $(NH_4)_2SO_4$, superphosphate and potassium sulphate.	Amount with respect to the N,P,K contents of wheat straw *i.e.* 67·44 lbs., 56·26 lbs. and 82·48 lbs. respectively.

Available phosphate was determined by Dyer's method (15). Exchangeable calcium was determined by Hissink's method (16). Dispersion factor (17), Permeability (18) and water holding capacity (19) also were determined.

The following abbreviations and connotations have been used throughout.

T.B.S. for Tata basic slag.
T.R.P. for Trichnopoly rock phosphate
T_0 for control
T_1 for T.B.S. treatment
T_2 for T.R.P. treatment
T_3 for KANS
T_4 for KANS + T.B.S.
T_5 for KANS + T.R.P.
T_6 for Coal
T_7 for coal + T.B.S.
T_8 for coal + T.R.P.
T_9 for Water hyacinth
T_{10} for Water hyacinth + T.B.S.
T_{11} for water hyacinth + T.R.P.
T_{12} for N + P + K.

TABLE 1

Analysis of the alkali soil and phosphatic amendments

% analysis	Soil	Tata basic slag	Trichinopoly rock phosphate
Moisture	1·52	–	–
Loss on ignition	2·7537	–	–
HCl insoluble	84·4250	22·5421	16·3628
Sesquioxides	6·8451	33·7438	26·6363
Fe_2O_3	3·9582	17·7816	4·2536
CaO	1·2408	22·4236	20·7514
MgO	1·0835	4·0462	0·9164
P_2O_5	0·1285	7·9238	26·6512
K_2O	0·7523	0·9158	0·0865
Available P_2O_5	0·0253	4·0724	2·5328
Total carbon	0·2201	–	–
Total Nitrogen	0·0401	–	–
NH_3——N	0·0019	–	–
NO_3——N	0·0028	–	–
pH	9·5	–	–
Conductivity	11·92 m.mhos/cm.	–	–
Mechanical composition of soil			
	%		
Coarse sand	9·85		
Fine sand	40·05		
Silt	26·82		
Clay	18·50		

TABLE (1*a*)

Analysis of organic materials

% analysis	KANS*	Water hyacinth	Coal
Loss on ignition	91·0266	71·3486	88·1356
Ash	8·9734	28·6514	11·8644
HCl insoluble	3·5765	–	4·4085
Sesquioxide	0·6813	–	1·1217
Fe_2O_3	0·3867	11·1316	0·6632
CaO	0·6693	2·7468	1·2427
P_2O_5	0·5312	3·1628	0·3128
K_2O	0·8986	0·6384	0·8654
MgO	0·6872	0·7582	1·4575
Total carbon	39·6357	26·9165	68·6328
Total Nitrogen	0·6796	1·4617	1·6685

*Sacchrum spontaneum

TABLE 2

The changes taking place in available P_2O_5, exchangeable calcium and physical properties of the soil under field

Analysis of the soil samples (Original)

Treat-ments	Available P_2O_5 %	Exch. Ca. m.e. %	Water holding capacity %	Permeabi-lity cc/hr	Dispersion factor %	pH	Electric conductivity m.mhos/cm
T_0	0·0253	2·50	47·3	4·00	15·50	9·50	11·92
T_1	0·0288	2·50	47·4	4·20	15·20	9·55	12·00
T_2	0·0285	2·50	47·4	4·20	15·20	9·55	12·00
T_3	0·0260	2·50	48·5	5·70	15·20	9·45	13·20
T_4	0·0252	2·50	48·6	5·70	14·90	9·50	14·50
T_5	0·0250	2·50	48·6	5·70	14·90	9·50	14·40
T_6	0·0253	2·50	48·4	6·00	15·30	9·50	13·20
T_7	0·0249	2·50	48·5	6·00	15·10	9·50	14·50
T_8	0·0247	2·50	48·5	6·00	15·00	9·50	14·50
T_9	0·0275	2·50	48·1	5·20	15·00	9·50	13·00
T_{10}	0·0260	2·50	48·2	5·20	14·80	9·50	14·00
T_{11}	0·0258	2·50	48·1	5·20	14·80	9·50	14·00
T_{12}	0·0245	2·50	47·3	4·00	15·45	9·50	12·25

TABLE 2 (*a*)

Analysis of the soil samples after 60 *days of treatments*

Treatments	Available P_2O_5 %	Exch. Ca. m.e. %	Water holding capacity %	Permeability cc/hr	Dispersion factor %	pH	Electric conductivity m.mhos/cm
T_0	0·0206	2·65	47·5	4·00	15·25	9·50	10·00
T_1	0·0331	2·72	47·7	4·40	13·35	9·50	8·86
T_2	0·0329	2·68	47·6	4·30	13·60	9·50	8·88
T_3	0·0272	3·20	50·0	14·20	11·50	8·80	8·50
T_4	0·0292	3·55	52·5	15·00	11·15	8·60	8·49
T_5	0·0289	3·45	50·1	14·80	11·25	8·65	8·50
T_6	0·0260	2·85	49·8	15·00	13·80	8·70	8·62
T_7	0·0273	2·95	52·0	16·00	12·80	8·55	8·52
T_8	0·0270	2·90	51·8	15·70	12·80	8·55	8·53
T_9	0·0325	2·75	49·5	12·50	13·00	8·85	8·75
T_{10}	0·0355	2·88	51·5	13·00	12·85	8·70	8·70
T_{11}	0·0352	2·82	51·0	12·80	12·90	8·75	8·71
T_{12}	0·0247	2·70	47·5	4·80	13·00	9·50	8·90

TABLE 2 (*b*)

Analysis of the soil samples after the harvest of the third crop (wheat)

Treatments	Available P_2O_5 %	Exch. Ca. m.e. %	Water holding capacity %	Permeability cc/hr	Dispersion factor %	pH	Electric conductivity m.mhos/cm
T_0	0·0142	2·50	49·0	6·50	12·55	8·50	7·20
T_1	0·0268	2·62	49·8	7·50	11·00	8·40	5·02
T_2	0·0266	2·60	49·5	7·50	10·90	8·45	5·05
T_3	0·0313	8·25	54·5	38·20	8·50	7·50	2·60
T_4	0·0343	14·00	56·5	43·50	7·15	7·20	2·08
T_5	0·0341	13·80	56·2	43·20	7·20	7·25	2·12
T_6	0·0302	8·30	54·4	38·20	8·10	7·45	2·50
T_7	0·0326	14·05	56·4	43·80	7·20	7·15	2·05
T_8	0·0324	13·85	56·0	43·50	7·25	7·20	2·08
T_9	0·0399	6·70	54·0	27·50	8·90	7·70	3·20
T_{10}	0·0417	11·85	56·0	31·40	7·80	7·50	2·65
T_{11}	0·0415	11·40	55·8	31·00	7·85	7·55	2·70
T_{12}	0·0262	2·85	49·0	9·80	11·80	8·40	5·40

Discussion

A careful perusal of the results recorded in Table 2 and 2(*a*) show that after 60 days of the incorporation of different organic materials *i.e.* KANS, coal and water hyacinth exchangeable calcium and available phosphate are considerably increased, the increase being more significants in systems phosphated with T. B. S. and T. R. P. Further comparison of these results with those obtained after the harvest of the third crop (wheat) and recorded in Table 2(*b*) shows that with the lapse of time the exchangeable calcium is markedly increased in the plots that have received different organic materials and phosphates. The plots receiving NPK do not show any significant change. In the 'Control' plots however a decrease in available P_2O_5 is recorded. Exchangeable calcium after the harvest of the wheat crops has the following decreasing order :

$T_7 > T_4 > T_8 > T_5 > T_{10} > T_{11} > T_6 > T_3 > T_9 > T_{12} > T_1 > T_2 > T_0$

The increase in the available phosphate and exchangeable calcium has been most satisfactorily explained by Dhar (15). He is of the opinion that during the slow oxidation of organic materials in soil carbonic acid and organic acids like acetic, citric and lactic acid etc. are produced which partly neutralise the alkalinity of the soils. Carbonic acid produced by the decomposition of organic matter plays an important role in soils. As is well known carbonic acid is much weaker an acid than phosphoric acid as is evident from their dissociation constants :

$$\frac{H^+ \times HCO_3^-}{H_2CO_3} = 3 \times 10^{-7} \quad \text{(First dissociation constant)}$$

$$\frac{H^+ \times CO_3^-}{HCO_3} = 6 \times 10^{-11} \quad \text{(Second dissociation constant)}$$

$$\frac{H^+ \times H_2PO_4^-}{H_3PO_4} = 1{\cdot}1 \times 10^{-2} \quad \text{(First dissociation constant)}$$

$$\frac{H^+ \times HPO_4^{--}}{H_2PO_4^-} = 2 \times 10^{-7} \quad \text{(Second dissociation constant)}$$

$$\frac{H^+ \times PO_4^{---}}{HPO_4^{--}} = 3{\cdot}6 \times 10^{-13} \quad \text{(Third dissociation constant)}$$

Because the dissociation constant of carbonic acid is much smaller than that of phosphoric acid, calcium carbonate is much more alkaline in its properties than calcium phosphate, although, the solubility of both these calcium salts at 0°C in water is practically the same as recorded in the following table :

Calcium carbonate $CaCO_3$	0·0013 at 0°C
Mono-calcium phosphate $Ca(H_2PO_4)_2\ H_2O$	4·0000 at 15°C
Dicalcium phosphate $CaHPO_4\ 2H_2O$	0·0289 at 0°C
Tricalcium phosphate $Ca_3\ (PO_4)_2$	0·0013 at 0°C

Thus carbonic acid attacks more readily the tricalcium phosphate and converts it into dicalcium phosphate and small amounts of mono calcium phosphate. The di- and mono- calcium phosphates react with sodium carbonate and bicarbonate present in the alkali soils and neutralise their alkaline property.

$$2NaHCO_3 + Ca(H_2PO_4)_2 = 2NaH_2PO_4 + Ca(HCO_3)_2$$
$$2NaHCO_3 + CaHPO_4 = Na_2HPO_4 + Ca(HCO_3)_2$$
$$Na_2CO_3 + Ca(H_2PO_4)_2 = 2NaH_2PO_4 + CaCO_3$$
$$Na_2CO_3 + CaHPO_4 = Na_2HPO_4 + CaCO_3$$

Consequently, the harmful effects of alkali carbonates are minimised due to the formation of sodium phosphates. Simultaneously, calcium bicarbonate produced in the system supplies soluble calcium ions along with mono calcium phosphate. Calcium ions thus brought into solution readily replace sodium ions on the exchange complex of the soil and increase the exchangeable calcium status of the soil, thereby, leading to the reclamation of the alkali soil.

The results recorded in Tables 2, 2(*a*) and 2(*b*) also reveal a marked increase in permeability in the plots after 60 days of the incorporation of KANS, coal and water hyacinth along with different phosphates. Also a steady increase in water holding capacity and a corresponding decrease in dispersion factor is observed. After the harvest of the wheat crop permeability is markedly enhanced in the plots receiving organic materials and phosphates. A maximum of 43·80 cc/hr in plot having coal and basic slag has been recorded as against 9·80 cc/hr and 6·50 cc/hr of the NPK plot and the 'Control' plot respectively. Similarly plots receiving energy materials and phosphates show a significant increase in the water holding capacity and a decrease in the dispersion factor after the wheat crop is harvested whilst NPK indicates no positive results.

Though after 60 days of the addition of different organic amendments the pH gets considerably lowered yet the decrease is remarkably significant after the third crop is harvested. The pH is lowered from 9·50 to 7·15 in the plots in which coal and Tata basic slag have been incorporated. The pH of the soil is markedly lowered by KANS and water hyacinth also, more so in the presence of basic slag and rock phosphate. NPK has an insignificant effect in lowering the pH over the 'Control'.

Soluble calcium and magnesium salts produced with the help of carbonic acid and other organic acids flocculate the soils and make the soil porous and, thereby, help leaching of the harmful soluble salts. The soluble salts have been observed to decrease considerably. Moreover, electric conductivity also is markedly decreased in the plots receiving organic materials and phosphates. Thus the pH is lowered and the alkali soil is reclaimed, moreover, in the nitrification of proteins and nitrogenous substances in the plant material, nitrous acid and nitric acid are produced which are also profitable in the reclamation of alkali soils.

From these investigations it can easly be concluded that waste materials like coal, KANS and water hyacinth when ploughed into alkali lands especially in presence of phosphates like basic slags or rock phosphates markedly increase available P_2O_5, exchangeable calcium, water holding capacity and permeability and decrease the dispersion factor and considerably lowers down the pH, hence, making the alkali land fertile and productive.

Summary

About two acres of uncultivated alkaline land of Phulpur (Allahabad) were reclaimed and made productive by incorporating waste carbonaceous materials like KANS (Sacchrum spontaneum), water hyacinth and coal at the rate of 5 tons/acre and phosphatic sources as Thomas slag and rock phosphate at the rate of 50 lbs P_2O_5/acre into the soil.

Three crops namely gram, paddy and wheat were grown over a period of about two years. The pH of the soil was reduced from 9·5 to 7·15 in the plots receiving coal and slag. By the incorporation of coal and other organic materials and phosphates the amount of soluble salts and electrical conductivity were appreciably reduced. Increase in available P_2O_5, exchangeable calcium, water holding capacity and permeability and a corresponding decrease in dispersion factor was observed when carbonaceous substances and phosphatic sources were ploughed in.

References

1. Govil, K. L. "Current Economic Problems" New Literature, Allahabad p. 61, 1948.
2. Raychaudhury, S. P. and Dutta Biswas, W. R. Saline and alkaline soils of Asia. *Trans. Vth. Inter. Cong. of soil Sc.*, **1** : 191–207, 1954.
3. Hissink, D. J. Rapporter met betrekking top de bodemgesteld-heid van de Wieringermeer en Vanden Andijker Proefpolder. *Ass. Repts.* 512, 1931.
4. Greene, H. and Snow, O. W. *J. Agri. Sci.* **29** : 1–34, 1939.
5. Kelley, W. P. *J. Agri. Sci.* **24** : 72, 1934.
6. Aramy, A. Die Verbessevung-smoglichkeiten bei ungarischn szikboden Pflernahr. **29** : 50–74, 1943.
7. Thomas, E. E. *Univ. Calif. Agri. Expt. Sta. Bull.* 601, 15, 1936.
8. Kelley, W. P. *Univ. Calif. Agri. Expt. Sta. Bull.* 617, 14, 1937.
9. Hilmy, M. *Proc. Midd. East Agri. Devel. Conference*, **48** : 51, 1944.
10. Singh, R. N. *Proc. Nat. Acad. Sci. India.* **25-A** : 211–227, 1955.
11. Dhar, N. R. *et al.* Prog. Rep. of the Scheme on Reclamation of saline and alkaline soils S. D. I. 1954–58, 1958.
12. Singh, P. N. *D.Phil. Thesis, Allahabad University*, 1960.

12(*a*). Banerji, N. K., *D.Phil. Thesis, Allahabad University*, 1960.

13. Sokolovsky, A. N. *et al. Dokl. Akad. S-kh. Nauk*, 7, 37–40, 1941.
14. Decoux, L. and Simon, M. *Inst. Belge Ame'lior Better., Publ.*, **13** : 173–185, 1945.
15. Dyer, B. *Trans. Chemi. Sec.* **65** : 115–67, 1934.
16. Hissink, D. J. *Soil Sci.* **15** : 269–76, 1923.
17. Puri, A. N. *Soils, Their Physics and Chemistry*, 113, 1949.
18. ——— *Proc. Soil Sci. Soc. Amer.*, **16** : 85–8, 1952.
19. Singh, R. *D.Phil Thesis, Allahabad University*, 1957.
20. Dhar, N. R. *Presid. Address, Nat. Acad. Sci. India*, **24-A** : 211–227, 1955.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968

A technique to study the mechanism of soil Compaction*

By

G. SRIRAMAMURTY

Officer Incharge, Tobacco Research Station, Pusa (Bihar)

Introduction

While there is general agreement on the effects of soil compaction on root and shoot growth and on nutrient uptake of plants there seems to be no definite conclusion about the exact mechanism by which plant growth is effected. Many workers (1, 3, 4, 6, 7) have expressed the difficulty in separating the effects of poor aeration from that of mechanical impedance to roots due to the fact that it is difficult to control the factors individually and measure the effects of each independantly. Gill and Miller (2) developed a technique for laboratory study of the influence of mechanical impedance and aeration on root growth of seedlings. A modified technique is described in this note.

Experimental set up

Alfalfa was selected for this study of soil compaction mechanism as the diameter of the root tips of this plant (as determined previously) was fairly constant upto five weeks after emergence of the seedling. Suction flasks of 600 ml. capacity were painted with black paint and were provided with corks. The corks were provided with two holes for two glass tubes to pass through. One of the glass tubes was connected to air supply (pressure pump) for aeration purposes. The other hole in the cork was for the capillary tube in which the alfalfa seedlings was grown.

For this purpose, pyrex capillary tubes of different sizes, each 7·5 cm. long, were prepared. Some of the capillary tubes were provided with bulbs of larger size than the capillaris, just half way in the glass tuber as per the following table :

Number of tubes	Size of capillary	Size of the bulb Diameter (1D) × Length in mm.
2	0·5	none
2	0·5	3 × 5
2	1·0	none
2	1·0	3 × 5
2	2·0	none
2	2·0	3 × 5
2	3·0	none
2	3·0	3 × 5

*Material forms part of Ph.D. thesis submitted to Kansas State University, U. S. A.

Young alfalfa seedlings, two days after germination were placed on these glass tubes with the tip of the radicle in the capillary. Nutrient solution from a central tank was dripped onto capillary tubes. The solution passed into the flask through the capillary tubes and out of the flask through the spout of the flask. About 500 ml. of the nutrient solution was passed through each flask each day. Aeration was provided constantly, throughout the experimental period.

After one month of growth, the root tips were measured and the fresh and dry weights of the roots and tops were recorded separately.

Discussion

The root tip diameters, the fresh weight and dry weight of roots and tops of alfalfa, grown in capillary tubes, are presented in Table.

TABLE

Diameter of root tips and weights of roots and tops.
(Average of two replications)

Size of Capillary	Diameter of root tip (mm) (1 mm from the tip)	Fresh weight (mg)			Dry weight (mg)		
		Roots	Tops	Total	Roots	Tops	Total
0·5 mm without bulb	(plants died after one week growth)						
0·5 mm with bulb*	0·25	2·0	19·0	21·0	1·0	4·2	5·2
1·0 mm without bulb	0·28	35·0	71·6	106·6	3·7	11·2	14·9
1·0 mm with bulb	0·25	15·1	29·9	55·0	2·4	5·1	7·5
2·0 mm without bulb	0·45	324·9	646·1	971·0	23·7	106·9	130·6
2·0 mm with bulb	0·43	174·5	320·1	494·6	13·5	58·2	71·6
3·0 mm without bulb	0·40	204·3	553·8	758·1	23·7	89·2	112·9
3·0 mm with bulb	0·50	138·3	366·0	504·3	15·4	58·9	74·3

* Only one plant survived.

When the plants were grown in 0·5 mm. diameter capillaries, three out of four plants died after one week. The fourth plant grown in 0·5 mm. capillary with a 3 mm. × 5 mm. bulb in the middle survived upto the end of the experiment (one month), though it did not put forth normal and healthy growth. Only 5·2 mg. of total dry weight was obtained.

The root tip diameter was increasing with increasing size of the capillary. The maximum size of the root tip was reached in the case of 3·0 mm. capillary provided with a bulb. This size (0·5 mm.) was very nearly the same as the size of the root tip when the plant was grown in sand (0·53 mm.) The diameter of the root tip was higher in capillaries not provided with the bulb except in the case of 3·0 mm. capillary. The results clearly indicated that the root tips were restricted from attaining normal size in the small size capillaries.

The maximum growth, both of roots and tops, was obtained in the case of 2·0 mm. capillary without the bulb. In all the cases, except 0·5 mm. capillary, capillary tubes provided with a bulb permitted less growth than when the capillaries were not provided with a bulb. This was possibly because of higher concentration of carbon dioxide in the bulbs than in the capillaries without the bulb. When the concentration of carbon dioxide around the root in the region of the bulb exceeds a limit, passage of corbohydrates and the growth of harmones from the leaves to the growing root tip would be limited. This probably accounted for the poor growth when the bulbs were provided in the capillaries.

This observation confirms the findings of Ohlrogge (5). He reported highest rate of elongation of roots in 1·0 mm. diameter capillaries (with maize) and the rate of elongation decreased with increasing tube diameter. He ascribed this to "wall effect".

Summary

A technique to separate the effect of poor aeration from that of mechanical impedance associated with soil compaction, on plant growth has been described.

Two days old alfalfa seedlings were grown, on capillary tubes of different sizes (0·5 to 3·0 m.m. diameter bores) kept in nutrient solution. The nutrient solution was aerated constantly throughout the experimental period. After one month growth, the root tip diameter was measured and the fresh and dry weights of the roots and tips were recorded separately.

The root tip diameter was increasing with increasing size of capillary ; the maximum size of 0·53 m.m. was obtained when the seedling was grown on 3·00 m.m. diameter tubes. This indicates that the root tips are restricted from attaining the normal size in the small size capillaries inspite of adequate aeration. The maximum growth, both of roots and tops, was obtained in the case of 2·00 m.m. capillary tubes.

The technique seems to be useful in separating the effects of mechanical resistance to roots from that of poor aeration.

References

1. Bertrand, A. R. and Kohnke, H. Sub-soil conditions and their effects on oxygen supply and the growth of corn roots. *Soil Sci. Soc. Amer. Proc.* **21** : 135-140, 1957.
2. Gill, W. R. and Miller, R. D. A method for study of influence of mechanical impedance and aeration on the growth of seedling roots. *Soil Sci. Soc. Amer. Proc.* **20** : 154–157, 1956.
3. Hanks, R. J. and Thorp, F. C. Seedling emergence of wheat as related to soil moisture content, bulk density, oxygen diffusion rate and crust strength. *Soil Sci. Soc. Amer. Proc.* **20** : 307–310, 1956.
4. Jamison, V. C. and Van Bavel, C. H. M. Nutrient uptake and chemical composition of tobacco plants as affected by the composition of root atmosphere. *Agron. Jour.* **49** : 176-181, 1957
5. Ohlrogge, A. J. Some soil-root-plant relationships. *Soil Sci.* **93** : 30–38, 1962.
6. Wicrsum, L. K. The relationship of the size and structural rigidity of pores to their penetration by roots. *Plant and Soil* **9** : 75-85, 1957.
7. Winters, Eric and Simonson Roy, W. The Sub-soil. *In* Advance in Agronomy **Vol. III**, 1-92. *Acadamic Press Inc. New York*, 1951.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968

Reclamation of Alkali Soil (II)

By

N. R. DHAR *and* A. K. RISHI

Sheila Dhar Institue of Soil Science, University of Allahabad, Allahabad (India)

Introduction

In Part I of these investigations it has been recorded that by ploughing in KANS (Sacchrum spontaneum), water hyacinth, coal and phosphates into alkali soil an increase in available P_2O_5, exchangeable calcium, water holding capacity and permeability and a corresponding decrease in pH, soluble salts, electric conductivity and dispersion factor is observed with lapse of time.

In this part the yields of gram, paddy and wheat grains and carbon and nitrogen status of the alkali soil after the incorporation of the above mentioned organic materials, Tata basic slag and Trichinopoly rock phosphate is discussed.

Methods and Materials

Composite soil samples after due intervals were analysed for organic carbon and total nitrogen. Carbon was determined by Schollenberger's method (1). Total nitrogen was estimated by sulphosalicylic acid reduction method (2).

The following abbreviations and connotations have been used throughout.

T.B.S. for Tata basic slag.
T.R.P. for Trichinopoly rock phosphate.
T_0 for control.
T_1 for T.B.S. treatment.
T_2 for T.R.P. treatment.
T_3 for KANS.
T_4 for KANS + T.B.S.
T_5 for KANS + T.R.P.
T_6 for Coal.
T_7 for Coal + T.B.S.
T_8 for Coal + T.R.P.
T_9 for Water hyacinth.
T_{10} for Water hyacinth + T.B.S.
T_{11} for Water hyacinth + T.R.P.
T_{12} for N + P + K.

TABLE 1

Percentage of total carbon

Treatments	Original	After 60 days	After gram harvest	After paddy harvest	After wheat harvest
T_0	0·2201	0·2198	0·1702	0·1660	0·1499
T_1	0·2195	0·1992	0·1665	0·1524	0·1369
T_2	0·2197	0·1987	0·1658	0·1527	0·1372
T_3	0·6802	0·6056	0·5502	0·5292	0·5092
T_4	0·6801	0·5830	0·5320	0·5007	0·4702
T_5	0·6801	0·5836	0·5324	0·5012	0 4708
T_6	1·0560	0·9950	0·7568	0·7370	0·7174
T_7	1·0554	0·9768	0·7328	0·7049	0·6775
T_8	1·0557	0·9770	0·7330	0·7052	0·6779
T_9	0·5001	0·4105	0·3254	0·3002	0·2752
T_{10}	0·4996	0·3958	0·3025	0·2672	0·2323
T_{11}	0·4997	0·3960	0·3030	0·2678·	0·2330
T_{12}	0·2201	0·2197	0·2154	0·1980	0·1820

TABLE 1 (*a*)

Percentage of total nitrogen

T_0	0·0400	0·0402	0·0388	0·0368	0·0350
T_1	0·0397	0·0413	0·0395	0·0380	0·0364
T_2	0·0398	0·0410	0·0390	0·0377	0·0362
T_3	0·0472	0·0495	0·0632	0·0655	0·0677
T_4	0·0467	0·0495	0·0665	0 0703	0·0735
T_5	0·0468	0·0518	0·0662	0·0702	0·0733
T_6	0·0545	0·0515	0·0582	0·0600	0·0616
T_7	0·0540	0·0549	0·0595	0·0630	0·0658
T_8	0·0542	0·0550	0·0590	0·0628	0·0656
T_9	0·0505	0·0568	0·0652	0·0654	0·0655
T_{10}	0·0500	0·0569	0·0660	0·0691	0·0719
T_{11}	0·0503	0·0568	0·0659	0·0689	0·0717
T_{12}	0·2655	0·2125	0·0305	0·0280	0·0257

TABLE 2

Yield of gram grain in Kgs

Treatments	Blocks				Total
	A	B	C	D	
T_0	0·9	0·6	0·8	0·7	3·0
T_1	1·0	1·2	1·0	1·0	4·2
T_2	1·1	0·8	0·9	0·7	3·5
T_3	4·1	3·8	4·2	4·0	16·1
T_4	6·0	5·4	5·8	5·5	22·7
T_5	4·8	4·4	5·0	4·6	18·8
T_6	3·8	3·0	3·6	3·1	13·5
T_7	5·5	4·3	5·0	4·7	19·5
T_8	4·5	3·8	4·2	4·0	16·5
T_9	1·7	1·0	1·1	1·0	4·8
T_{10}	2·5	1·9	2·3	2·0	8·7
T_{11}	1·8	1·2	1·6	1·4	6·0
T_{12}	1·4	1·0	1·2	1·0	4·6

TABLE 3

Analysis of variance of yield data of gram grain

Factors	D. F.	S. S.	M. S. S.	Calculated F	Expected F		Level of significance
					1 %	5 %	
Treatments	12	147·15	12·26	87·5	2·72	2·03	Highly significant
Blocks	3	2·10	0·70				
Error	36	4·94	0·14				
Total	51						

TABLE 4

Yield af paddy grain in Kgs

Treatment	Blocks				Total
	A	B	C	D	
T_0	1·6	1·8	1·2	1·4	6·0
T_1	2·2	2·5	2·4	2·2	9·3
T_2	1·8	2·0	2·2	2·0	8·0
T_3	7·5	7·7	7·8	7·2	30·2
T_4	9·5	9·6	9·8	9·6	38·5
T_5	8·8	9·0	8·9	8·6	35·3
T_6	7·4	7·6	7·4	7·6	30·0
T_7	9·0	9·4	9·8	9·0	37·2
T_8	9·0	8·2	9·0	8·8	35·0
T_9	4·0	4·2	3·8	4·5	16·5
T_{10}	5·8	6·0	6·2	6·2	24·2
T_{11}	5·7	5·5	6·0	5·8	23·0
T_{12}	3·0	2·8	3·2	3·0	12·0

TABLE 5

Analysis of variance of yield data of paddy grain

Factors	D. F.	S. S.	M. S. S.	Calculated F	Expected F		Level of significance
					1 %	5 %	
Treatments	12	425·36	35·45	709·0	2·72	2·03	Highly significant
Blocks	3	0·24	0·08				
Error	36	1·95	0·05				
Total	51						

TABLE 6

Yield of wheat grain in Kgs

Treatments	Blocks				Total
	A	B	C	D	
T_0	1·3	1·6	1·4	1·2	5·5
T_1	2·4	2·1	2·3	2·2	9·0
T_2	1·8	1·6	2·0	1·8	7·2
T_3	7·2	7·0	7·3	7·5	29·0
T_4	9·2	9·0	9·8	9·6	37·6
T_5	8·8	8·6	8·4	8·2	34·0
T_6	7·0	6·9	7·5	7·1	28·5
T_7	9·2	9·0	9·4	8·6	36·2
T_8	8·2	8·6	8·5	8·2	33·5
T_9	3·8	4·0	3·5	3·7	15·0
T_{10}	5·3	5·8	5·9	6·0	23·0
T_{11}	5·4	5·6	5·0	5·5	21·5
T_{12}	2·8	2·4	3·0	2·8	11·0

TABLE 7

Analysis of variance of yield data of wheat grain

Factors	D. F.	S. S.	M. S. S.	Calculated F	Expected F		Level of significance
					1%	5%	
Treatments	12	410·28	34·19	488·4	2·72	2·03	Highly significant
Blocks	3	0·16	0·05				
Error	36	2·54	0·07				
Total	51						

Discussion

There is a gradual oxidation of carbon in all the plots receiving KANS, coal and water hyacinth, and this oxidation is markedly enhanced in the plots having

these organic materials along with Tata basic slag and Trichinopoly rock phosphate (Vide table 1). Correspondingly an increase in total nitrogen in the plots having organic materials is observed, the increase being more pronounced in the phosphated plots (Vide table 1*a*). These observations clearly show that the energy released during the oxidation of organic materials is utilised in fixing atmospheric nitrogen. The nitrogen fixation, in all the plots receiving organic materials and phosphates, continues till the harvest of the third crop (wheat). On the contrary plots receiving NPK show a constant loss of nitrogen.

From a careful perusal of tables 1 and 1*a* it can be observed that even after the harvest of third crop *viz.*, wheat the percentage of total carbon in the plots receiving KANS and coal are much higher as compared to the 'Control' plots or the plots receiving NPK. Maximum residual effect is observed in the plots having coal. The percentage of carbon after the harvest of wheat is 0·7174 in coal receiving plot against 0·5092 and 0·1820 of the plots receiving KANS and NPK respectively, and 0·1499 of the 'Control'.

The maximum percentage of nitrogen *viz.*, 0·0735 observed after the harvest of the third crop is in the plots receiving KANS+T. B. S. Plots receiving water hyacinth and coal also show more or less similar gains of nitrogen, the increase being pronounced in the plots having organic materials along with phosphates.

The yield of gram grain and the analyses of variance of the yield data are recorded in Tables 2 and 3. Apparantly there is significant difference between the yields with different treatments. The results obtained show that the calculated value of F for grain is 87·5 which is highly significant at 1% and 5% level of significance.

The yield data of paddy grain and the analyses of variance are recorded in Tables 4 and 5 respectively. And the yield data of wheat grain and the analyses of the variance of yield data are recorded in Tables 6 and 7. The calculated values of F for paddy grain and wheat grain are 709·0 and 488·4, both of which are highly significant at 1% and 5% level of significance. Moreover, different treatments show significant difference in yields of paddy and wheat grain.

From these investigations it can conveniently be emphasised that waste organic materials, like KANS (Sacchrum spontaneum), coal, water hyacinth etc., and slags and rock phosphates can be profitably utilised in reclaiming vast areas of alkaline land and making them productive.

Summary

In this part the yields of gram, paddy and wheat grains along with the carbon and nitrogen status of the alkali soil after the incorporation of KANS, coal, water hyacinth, Tata basic slag and Trichinopoly rock phosphate is discussed.

Observations indicate that the nitrogen status of the soil is markedly enhanced by the slow oxidation of energy materials and, that along with reclaiming the alkali soil bumper crops have been grown on the land.

From these investigations it is concluded that easily available carbonacious materials like KANS, coal etc., and slags and rock phosphates can be profitably utilised in reclaiming millions of acres of alkaline soils prevalent in India and, thereby, the food shortage of the country can be considerably reduced.

References

1. Schollenberger, C. J. *Soil Sci.*, **59** : 53, 1945.
2. Treadwell, F. P. and Hall, W. T. *Analytical Chemistry*, **11** : 493–4, 1947.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968

Solubilization of Calcium and Magnesium Phosphates by Various Aliphatic Acids

By

N. R. DHAR, R. C. KAPOOR *and* M. K. FOTEDAR

Sheila Dhar Institute of Soil Science, University of Allahabad, Allahabad

Introduction

The nutrient value of the phosphates for the plants cannot be correlated completely with their solubility tests in water. It is generally believed that phosphates readily soluble in water are suitable for rapid plant growth, but, dicalcium phosphate which is sparingly soluble in water, is excellent crop improver and is fairly soluble in citric acid. The value of phosphatic fertilizers as sources of phosphorus for plants depends upon many soil properties and the availability of phosphorus in the products formed as a result of the reaction between the fertilizers and soils (1-3).

It has been reported by various workers (4 and 5) that in soils rich in organic matter, there is always appreciable production of weak organic acids like, citric, tartaric, acetic, lactic etc. which react with the phosphate and thus give an indication of the availablity of the phosphate.

In the present investigation the solubilizing action of various aliphatic acids like citric, tartaric, formic, lactic, acetic and butyric on calcium and magnesium phosphates has been studied as these phosphates are believed to be the main suppliers of phosphate in the soil. Since the exact nature of these phosphates in the soil is yet unknown, laboratory samples were utilized for the experimental purposes.

Experimental

Calcium and magnesium phosphates used in these experiments were prepared in the laboratory and the analysis showed them to have compositions corresponding to the formulae, $CaHPO_4 . 2H_2O$, $Ca_3(PO_4)_2 . 5H_2O$, $MgHPO_4 . 7H_2O$ and $Mg_3(PO_4)_2 . 8H_2O$. The various aliphatic acids used were of A. R. Grade. Throughout the experiment 0·1 N acid solutions were employed and the experiments were performed at 30°C.

1 gm. each of the precipitated phosphates was taken in Jena glass bottle and to this 100 ml. of 0·1 N acid solution was added. The bottle containing the phosphate-acid mixture was shaken on a mechanical shaker for 2 hours. The mixture in the bottle was then allowed to settle, and filtered to give a clear filtrate.

The P_2O_5 content of the filtrate was determined after oxidising the organic matter present in it by repeated evaporation with concentrated nitric acid and subsequent precipitation with ammonium molybdate (6).

Results

TABLE 1

Solubility of Calcium and Magnesium phosphates in various aliphatic acids

Acid used	$CaHPO_4 2H_2O$	$Ca_3(PO_4)_2.5H_2O$	$MgHPO_4.7H_2O$	$Mg_3(PO_4)_2.8H_2O$
	P_2O_5 dissolved in millimoles/litre			
Citric acid	23·45	20·36	25·61	22·43
Tartaric acid	21·15	16·66	22·67	18·72
Formic acid	16·57	13·01	18·43	15·23
Lactic acid	10·67	8·76	13·56	10·56
Acetic acid	6·80	5·59	8·20	6·96
Butyric acid	4·82	4·04	5·71	5·01

Discussion

The experimental results show that the solubility of all the calcium and magnesium phosphates increases markedly in presence of weak aliphatic acids. Though all these phosphates are soluble to different extents in these organic acids, yet a general regularity is observed regarding the solubility. On the basis of their dissolving action these acids can be arranged as below :

Citric > Tartaric > Formic > Lactic > Acetic > Butyric

The results point out that magnesium phosphates are more soluble than the corresponding calcium phosphates in presence of these organic acids and also indicate that the solubility of their di-phosphates is greater than the corresponding tri-phosphates.

These results on the P_2O_5 solubility of these phosphates in different organic acid solutions indicate that the organic acids can extract greater amounts of phosphoric acid from soils rich in calcium and magnesium phosphates than from soils rich in iron and aluminium phosphates. Moreover, the increased available status of soils in which calcium phosphates are supplemented with decomposing organic matter can be attributed to the above phenomena. Dalton *et al* (7) have reported the formation of weak organic acids during the decomposition and oxidation of organic substances in the soil.

The relative solubilizing action of the various aliphatic acids can be attributed to the following considerations :

Dissociation constants of these acids at 25°C (8, which are as given below :

Citric acid	K_1	$8{\cdot}7\times10^{-4}$
	K_2	$1{\cdot}8\times10^{-5}$
	K_3	$4{\cdot}4\times10^{-6}$
Tartaric acid	K_1	$9{\cdot}6\times10^{-4}$
	K_2	$2{\cdot}9\times10^{-5}$
Formic acid	K	$1{\cdot}77\times10^{-4}$
Lactic acid	K	$1{\cdot}4\times10^{-4}$
Acetic acid	K	$1{\cdot}75\times10^{-5}$
Butyric acid	K	$1{\cdot}5\times10^{-5}$
Phosphoric acid	K_1	$7{\cdot}5\times10^{-3}$
	K_2	$6{\cdot}2\times10^{-8}$
	K_3	$4{\cdot}8\times10^{-13}$

The second and the third dissociation constants of phosphoric acid are less than the total dissociation constants of all the organic acids employed in this investigation. The H^+ ions available from these acids facilitate the formation of $H_2PO_4^-$ and HPO_4^{-2}, thus rendering the sparingly soluble phosphates of calcium and magnesium more soluble.

$$PO_4^{-3} + H^+ = HPO_4^{-2} \quad (1)$$

$$HPO_4^{-2} + H^+ = H_2PO_4^- \quad (2)$$

It may be concluded that the reaction of organic acids with these phosphates is one of acid dissociation. The amount of phosphate released depending mainly on the strength of the acid. When dibasic and tribasic acids are used, a secondary effect appears due to the ability of these acids to form complex compounds. This makes the reaction go further and increase the phosphate brought into the solution.

The structural characteristics of the organic anion also seem to be of importance in adding to the solubility of these sparingly soluble phosphates, apart from the influence of H^+ ion concentration, Johnston (9) remarked that the ability of a large number of organic acids in dissolving calcium phosphate and hydroxyapatite clearly indicated that the reaction is not solely dependent on the pH of the solution used, but, that is also dependent on the structural characteristics.

Summary

It has been observed that the solubility of all the calcium and magnesium phosphates increases markedly in presence of various aliphatic acids. On the basis of their solubilizing action on these phosphates, these acids can be arranged in the following order :

Citric > Tartaric > Formic > Lactic > Acetic > Butyric

It has also been noticed that the action of these acids is not merely dependent upon the strength of the acids, but it is also dependent upon their structural characteristics and that is why citric acid has been found to cause maximum solubility of these phosphates.

Acknowledgements

Authors (R. C. K. and M. K. F.) are grateful to the Government of India, Ministry of Education and University of Allahabad for financial assistance.

References

1. Dean, L. A. *Advances in Agron.* **1** : 391–411, 1949.
2. Midgely, A. R. *Soil Sci. Soc. Amer. Proc.*, **5** : 24 30, 1941.
3. Wild, A. *J. Soil Sci.*, **1** : 221–238, 1950.
4. Dhar, N. R. *et al. Phosphorsaeure*, **21** : 233–247, 1961 ; *Proc. Nat. Acad. Sci., India*, **25A** (4), 1956 ; *Agri. Digest No.* 7, 3–7, 1966.
5. Ilyaletdinov, A. N., Mamilov, Sh. and Berezina, F. S. *Izv. Akad. Nauk., Ser. Biol.*, **3** (1) : 52–57, 1965.
6. Vogel, A. I. A Text Book of Quantitative Inorganic Analysis, *Longman's Green and Co., London*, 2nd ed., 1958.
7. Dalton, *et al. Soil Sci.* **73** : 173–181, 1952.
8. Lange, N. A. *Compare Hand Book of Chemistry, McGraw-Hill Book Co., Inc.*, 1198-1202, 1961.
9. Johnston, H. W. *New Zealand J. Sci. Tech.*, **33B**, 436, 1952.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968.

Effect of washing on some sparingly soluble phosphates

By

N. R. DHAR, G. N. PANT & M. K. FOTEDAR

Sheila Dhar Institute of Soil Science, University of Allahabad, Allahabad

The solubility of various sparingly soluble phosphates in water is one of the most important factors that influence the ability to supply phosphorus to plants. Among all the phosphates present in the soil, calcium phosphate is the most important which determines the availability of the phosphate. Iron and aluminium phosphates also play a significant part in the release of phosphate in the soil solution. This release of phosphate in to the solution is believed to be brought about due to hydrolysis. Rindell (1), Cameron and Hurst (2) and Cameron and Bell (3) have shown that phosphates are hydrolysed in presence of water and the amount of phosphoric acid passing in to solution is influenced by a number of factors.

A number of workers (4-7) have reported that calcium phosphates are decomposed by water to form free phosphoric acid. Klement (8) and Cameron and Bell (9) have reported that magnesium phosphates also decompose in contact with water and liberate free phosphoric acid. Cameron and Hurst (2) observed that phosphates of iron and aluminium also hydrolyse in to phosphoric acid and their respective hydroxides. Ferrous and titanium phosphates do not hydrolyse to an appreciable extent.

Since the exact nature of the phosphates of calcium, magnesium, iron, aluminium and titanium in soils is yet unknown which are supposed to be the main suppliers of phosphate to the plants, the present study was, therefore, undertaken to investigate the washing of all these sparingly soluble phosphates.

Experimental

The phosphate samples used in these experiments were prepared in the laboratory. Analysis showed them to have a composition corresponding to the formulae, $CaHPO_4$, $CaHPO_4.2H_2O$, $Ca_3(PO_4)_2$, $MgHPO_4.3H_2O$, $Mg_3(PO_4)_2$, $FePO_4.2H_2O$, $Fe_3(PO_4)_2.8H_2O$, $AlPO_4.H_2O$ and $Ti_3(PO_4).6H_2O$. 1 gm each of these phosphate samples was taken in a conical flask and 100 ml of distilled water added to it. The contents were shaken for 2 hours on a mechanical shaker and left to stand for 24 hours in a Thermostat maintained at a temperature of 30°C. At the end of this time, the contents were filtered. Aliquot portions of the filtrate were taken for the determination of P_2O_5, pH and electrical conductivity. The residue was transferred to the flask and the volume made up to 100 ml and similar procedure was followed as in the previous case for the subsequent washings after every 24 hours.

In the case of calcium, magnesium, ferric aud aluminium phosphates, P_2O_5 was determined by precipitation method (10). Colorimetric method (11) was employed for the P_2O_5 estimation in the case of ferrous and titanium phosphates. pH of the solutions was determined by portable Cambridge pH meter and the electrical conductivity was measured by "Leitfahigkeitnsmesser" conductivity bridge (Laboratory model, S. No. 77), which is operated by mains.

Resuls

TABLE 1(*a*)

P_2O_5 millimoles per litre

Number of the washing	$CaHPO_4$	$CaHPO_4.2H_2O$	$Ca_3(PO_4)_2$	$MgHPO_4.3H_2O$	$Mg_3(PO_4)_2$
1	0·3512	1·4387	1·0368	3·0620	1·9835
2	0·3081	1·3015	0·7479	2·0108	1·6827
3	0·2573	1·1194	0·6141	1·8742	1·3933
4	0·2447	0·9805	0·5685	1·4534	1·3080
5	0·2281	0·8473	0·5408	1·0969	1·1628
6	0·1903	0·6902	0·5310	0·8009	0·9156

TABLE 1(*b*)

pH

1	7·60	6·70	5·80	7·55	7·45
2	7·65	6·75	6·05	7·55	7·55
3	7·65	6·80	6·15	7·60	7·60
4	7·70	6·85	6·30	7·65	7·70
5	7·75	6·90	6·50	7·70	7·75
6	7·80	6·95	6·80	7·75	7·80

TABLE 1(*c*)

Specific conductivity in mhos $\times 10^{-4}$

1	1·88	3·60	2·64	5·26	3·85
2	1·67	3·12	2·19	4·53	3·36
3	1·59	2·73	1·95	4·07	2·90
4	1·50	2·40	1·86	3·62	2·50
5	1·40	2·01	1·60	3·15	2·09
6	1·28	1·59	1·37	2·40	1·72

TABLE 2(*a*)

P_2O_5 millimoles per litre

Number of the washing	$FePO_4.2H_2O$	$Fe_3(PO_4)_2.8H_2O$	$AlPO_4.H_2O$	$Ti_3(PO_4)_4.6H_2O$
1	0·3255	0·0684	0·6653	0·0102
2	0·2145	0·0628	0·4997	0·0101
3	0·1709	0·0589	0·3923	0·0100
4	0·1203	0·0581	0·3084	0·0098
5	0·0986	6·0563	0·2126	0·0097
6	0·0817	0·0559	0·1070	0·0096

TABLE 2(*b*)

pH

1	6·90	6·85	7·35	6·30
2	6·90	6·85	7·45	6·30
3	6·95	6·85	7·50	6·30
4	7·00	6·90	7·55	6·30
5	7·05	6·90	7·55	6·30
6	7·15	6·95	7·65	6·35

TABLE 2(*c*)

Specific conductivity in mhos $\times^{-4}$

1	1·08	0·36	2·18	0·04
2	0·94	0·34	1·89	0·04
3	0·82	0·33	1·61	0·04
4	0·73	0·30	1·42	0·03
5	0·61	0·29	1·20	0·03
6	0·45	0·26	0·79	0·03

Discussion

From a study of the experimental results recorded in the tables 1(*a*) to 2(*c*), the effect of washing on the P_2O_5 solubility and the pH and electrical conductivity of the corresponding solutions of the phosphates of calcium, magnesium, ferrous, ferric, aluminium and titanium becomes evident. In general all these sparingly soluble phosphates are hydrolysed by water liberating small amount of phosphoric acid.

Anhydrous dicalcium phosphate has been found to be less soluble than tricalcium phosphate, whilst dihydrated dicalcium phosphate is more soluble than tricalcium phosphate. Therefore, it seems that dihydrated dicalcium phosphate is likely to be present in greater amounts, when soils are phosphated by superphosphate, finely divided rocks or basic slags. Many workers (12-14) have shown that when concentrated superphosphate or monocalcium phosphate is applied to soils, dihydrated dicalcium phosphate is one of the major products formed. But in the course of time due to the presence of fluorine in all the soils, the calcium phosphates are converted in to very sparingly soluble fluorapatites.

Like calcium, magnesium hydrophosphate – trihydrate is more soluble than tri-magnesium phosphate. Among all the phosphates studied magnesium phosphates, have been found to be most soluble and conducting in water.

Ferric and aluminium phosphates liberate much more amount of P_2O_5 in to the solution than ferrous and titanium phosphates. The amounts of P_2O_5 passing in to the solution with ferrous, ferric and titanium phosphates are less than all the calcium and magnesium phosphates and with aluminium phosphate less than all these phosphates except anhydrous dicalcium phosphate. Hence it is evident from the results that even the so-called sparingly soluble phosphates of iron, aluminium are also moderate suppliers of phosphate together with more soluble calcium and magnesium phosphates. The residual effect of phosphates reported by Scarseth and Chandler (15), Volk (16) and Ensminger and Cope (17) and the increase in the availibility of phosphate as reported by Shapiro (18), Fujiwara (19) and Mitsui (20) under flooded soils than under unflooded conditions also appears to be a consequence of hydrolysis.

It has been observed that the P_2O_5 concentration in various extracts shows a gradual decrease from the first extraction to the sixth. The electrical conductivity also likewise decreases in the various extracts which may be due to the fact that lesser number of ions are passing in to the solution. With ferrous and titanium phosphates the amount of P_2O_5 passing in to the solution changes very slightly. In the sixth extract of ferric and aluminium phosphates the amounts of P_2O_5 decrease nearly to four and six and a half times of the first extract respectively. In the cases of calcium, magnesium, ferric and aluminium phosphates, the H^+ concentration of the successive extracts decreases indicating that basic phosphates are being formed which contain more of the basic oxide than P_2O_5. With ferrous and titanium phosphates the change in pH is not significant which may be due to the fact that the P_2O_5 concentration in the various extracts does not change appreciably.

It is evident from the results that even after the sixth extraction appreciable amount of P_2O_5 goes in to the solution with calcium, magnesium, ferric and aluminium phosphates indicating that there is a great chance of the added phosphate being lost by leaching in drainage water in areas of large rainfall. The results further indicate that the loss of phosphate will be much more in soils containing calcium and magnesium phosphates than in soils containing iron, aluminium and titanium phosphates. These conclusions are in close agreement

with the observations of Dhar and Misra (21) who have reported that greater amount of phosphate is leached out when the soils are richer in calcium phosphates. This washing away of phosphates from soils seems to be an important factor in causing the low recovery of phosphate by the crops.

Summary

It has been observed that the phosphates of calcium, magnesium, iron, aluminium and titanium are hydrolysed by water liberating small amounts of phosphoric acid. The results show that even the so-called sparingly solubly phosphates of iron and aluminium are also moderate suppliers of phosphate together with more soluble calcium and magnesium phosphates.

The P_2O_5 concentration in various extracts shows a gradual decrease from the first extraction to the sixth and even after the sixth extraction considerable amount of P_2O_5 goes in to the solution. The results indicate that the loss of phosphate will be much more in soils containing calcium and magnesium phosphates than in soils containing iron, aluminium and titanium phosphates.

References

1. Rindell, A. *Compt. Rend.*, **134** : 112, 1902.
2. Cameron, F. K. and Hurst, L. A. *J. Amer. Chem. Soc.*, **26** : 885, 1904.
3. Cameron, F. K. and Bell, J. M. *U. S. Dept. Agr., Bureau of Soils, Bull.*, 41, 1907.
4. Cameron, F. K. and Seidell, A. *J. Amer. Chem. Soc.*, **26** : 1454, 1904.
5. Koch, E. and Wrangel, M. Von. *Landw. Jahrb.*, **63** : 677-706, 1926.
6. Raistrick, B. and Rickso, J. B. *Joint Tech. and Agr. Meeting, Lausane (Switzerland). Association Internationale des fabricants de Superphosphate- (I. S. M. A.)* 1956.
7. Montel, G. *Bull. Soc. Chim.*, 506-11, 1953.
8. Klement, R. *Z. anorg. u. allgem. Chem.*, **228** : 232, 1936.
9. Cameron, F. K. and Bell, J. M. *J. Phys. Chem.*, **11** : 363, 1907.
10. Vogel, A. I. A Text Book of Quantitative Inorganic Analysis, *Longman's Green & Co., London,* IInd Edition, 1958.
11. Snell, F. D. and Snell, C. T. Colorimetric Methods of Analysis, *D. Van Nostrand Co., Inc., New York,* Vol. I : 1937.
12. Lehr, J. R., Brown, W. E. and Brown, E. H. *Soil Sci. Soc. Amer. Proc.*, **23** : 3-7, 1959.
13. Lindsay, W. L. and Stephenson, H. F. *ibid.*, **23** : 440-445, 1959.
14. Lehr, J. R. and Brown, W. E. *ibid.*, **22** : 29-32, 1958.
15. Scarseth, G. D. and Chandler, W. V. *J. Am. Soc. Agron.*, **30** : 361-74, 1938.
16. Volk, G. W. *ibid.*, **37** : 330-40, 1945.
17. Ensminger, L. E. and Cope, J. T. *ibid.*, **39** : 1-11, 1947.
18. Shapiro, R. E. *Soil Sci.*, **85** : 190, 1958.
19. Fujiwara, A. *Tohoku J. Agric. Res.*, **1** : 129, 1950.
20. Mitsui, S. *Inorganic Nutrition, Fertilization and Soil Amelioration for Low Land Rice. Yokendo Ltd., Tokyo, Japan,* 1954.
21. Dhar, N. R. and Misra, S. G. *Proc. Nat. Acad. Sci., India,* **25A** : 420-432, 1956.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968

Nitrogen loss in soil - effect of organic matter and Phosphate

By

N. R. DHAR, S. P. JAISWAL & A. K. RISHI

Sheila Dhar Institute of Soil Science, University of Allahabad, Allahabad

Introduction

Increased use of fertilizers is one of the most important means of augmenting the yield of food crops and in this connection nitrogen fertilizers play a special role. On the application of nitrogenous fertilizers to the soil, however, whole of their nitrogen content is not utilized by the plant but a good deal of it is lost through leaching, denitrification, and volatalisation. Under field conditions recovery of inorganic nitrogen seldem exceeds 50% (Russell, 1950 ; Mac Vicar *et al*, 1951, Bartholomew *et al*, 1952). Harmsen and Vanschrewen (1955) and Allison (1955) reviewed the pertinent literature and recommended use of straw and saw dust etc. for preventing nitrogen losses from soil. It has also been observed (Crowther, C. M. and Yates F., 1941 ; Russell, 1950 ; Dhar, 1955) that when nitrogenous fertilizers were added along with potassium salts and/or with phosphate salts, the loss of nitrogen from nitrogenous fertilizers decreases markedly and the response of crops in terms of yields is better as compared to when nitrogenous fertilizers are used alone. In this paper an attempt has been made to study the effect of wheat straw and German basic slag on conservation of fertilizer nitrogen in the soil.

Experimental

The collected soil was passed through 100 mesh sieve after drying in air. Its chemical composition and mechanical analysis was carried out by the methods described by Piper (1947) and A. O. A. C. (1945). Wheat straw and German basic slag were finely ground so as to pass through 10 mesh and 100 mesh sieve respectively. Two Kilograms of soil were filled in each of the required number of pots and the treatments shown in the table 2 were set up. Organic material, ammonium sulphate and slag were used at the rate of 2000 ppm carbon, 100 ppm. nitrogen and 50 ppm P_2O_5 respectively. Throughout the experiment moisture content was maintained at 40% of water holding capacity by adding distilled water daily. The mean average temperature during the course of the experiment was 30°C. After definite intervals of time composite soil samples were drawn and analysed. Total nitrogen was determined by the Kjeldahl salicylic acid reduction method to include nitrate nitrogen (John-Brooks, 1936). Ammonium nitrogen was determined by the method of Shrikhande (1943) and nitrate nitrogen by phenol disulphonic acid method.

Results

TABLE 1

Composition of soil and amendments

Analysis of Soil

Loss on Ignition	2·96	*Mechanical Analysis*	
Nitrogen		Sand	64·9%
Ammonium	0·0012%	Salt	14·5%
Nitrate	0·0017%	Clay	19·9%
Total	0·0348%	*HCl Extract analysis*	
Total Carbon	0·253%	HCl insoluble	81·20%
C/N	7·2	R_2O_3	11·05%
pH	7·6	Fe_2O_3	4·98%
E. E. C.	12·6 me/100 gm. soil	CaO	1·42%
Exch. Ca	5·1 me/100 gm. soil	MgO	1·01%
Available P_2O_5	14 ppm	K_2O	1·04%
		P_2O_5	0·11%

Analysis of Wheat Straw and German basic slag

Wheat Straw		*German basic slag*	
Total Carbon	39·61%	Total P_2O_5	17·90%
Total Nitrogen	0·41%	Available P_2O_5	9·396%
C/N	96·6	CaO	33·55%
		K_2O	1·05%

TABLE 2

Effect of Wheat straw and German basic slag on nitrogen loss and available nitrogen contents in soil

Treatments	Total Nitrogen in ppm				Ammoniacal Nitrogen in ppm				Nitrate Nitrogen in ppm				Changes in N contents in 75 days		
	Period in days				Period in days.				Period in days						
	0	15	45	75	0	15	45	75	0	15	45	75	Total-N	Ammoniacal-N	Nitrate-N
1. Soil alone	348	354	356	347	12	18	25	19	17	21	32	29	−1	+7	+12
2. Soil+Amm. sulphate	442	422	418	416	107	62	44	40	18	62	81	70	−26	−67	+52
3. Soil+Amm. Sulphate+Slag	440	427	422	421	109	62	45	38	18	65	86	78	−19	−71	+60
4. Soil+Straw	353	370	362	382	8	13	25	36	17	3	12	28	+29	+28	+11
5. Soil+Straw+ Amm. sulphate	450	459	472	472	106	79	66	56	15	38	54	65	+22	−50	+50
6. Soil+Straw+ Slag	353	375	390	395	9	17	30	40	14	4	20	38	+42	+31	+24
7. Soil+Straw+Amm. Sulphate+Slag	452	460	475	478	106	75	69	59	16	42	61	70	+26	−47	+54

Discussion

Results recorded in Table 2 show that when ammonium sulphate is added to the soil it suffers loss. The loss is very quick in the beginning but the rate shows down with time. As reflected by the total nitrogen values addition of wheat straw to the system not only conserves inorganic nitrogen but also favours nitrogen fixation. The results are in agreement with those of Chandra and Bollen (1959) who recorded nitrogen fixation even in presence of nitrogenous fertilizers with the addition of straw and saw dust.

An increase in total nitrogen values by addition of straw may be due to suppression of denitrification and fixation of atmospheric nitrogen by biological and physico-chemical agencies, the oxidation of energy material providing energy for the endothermic process (Dhar, 1955, Mc Garity *et al*, 1958 ; Chandra *et al*, 1957). Bremmer and Shaw (1959) while studying the effect of energy materials on reduction of nitrates observed that maximum loss occurred with glucose and nitrate at C : N ratio of 5 : 1, with straw and nitrate at C : N ratio of 30 : 1 and with wider ratio loss of nitrogen decreased due to nitrogen fixation. Addition of wheat straw with wide C : N ratio and with the resultant widening of C : N ratio of the mixture might have been helpful in nitrogen fixation.

Addition of phosphate in the form of German basic slag has markedly reduced the nitrogen loss and increased nitrogen fixation. This action of phosphate has been explained by Dhar (1955) from the view point that during the process of ammonification and nitrification of proteins a highly unstable intermediate product, ammonium nitrite is formed (Proteins $\xrightarrow{}$ amino acids $\xrightarrow{+O_2}$ ammonium compounds $\xrightarrow{+O_2}NO_2\xrightarrow{+O_2}NO_3$). It readily decomposes forming water and nitrogen gas with marked evolution of heat. This, alongwith nitrogen fixation and formation of proteins caused by the absorption of energy obtained from oxidation of organic materials, ammonification and nitrification of nitrogenous compounds which opposes the increase of proteins in the system, takes place and thus the amount of protein tends to decrease. But in the presence of phosphates more or less stable phospho-proteins are formed by the combination of proteins and phosphate (Dhar and Ghosh, 1956). These compounds seem to resist ammonification, nitrification and loss of nitrogen more than proteins alone. Moreover, basic slags also supply calcium and magnesium ions in the system to form calcium and magnesium nitrites which are more stable than ammonium nitrite with the result nitrogen of the system is conserved.

Ammoniacal and nitrate nitrogen values recorded in Table 2 show that with the addition of straw there is temporary exhaustion of available nutrients. This appears to be due to the assimilation of available nitrogen by rapidly multiplying microorganisms on added energy source. Subsequent increase in available nitrogen was as a result of mineralisation of immobilized nitrogen. Higher percentage of available nitrogen in presence of basic slag seems to be due to the increased decomposition and oxidation of organic matter and reduced loss of mineralised nitrogen (Jaiswal, 1964).

Summary

Effect of organic matter in the form of Wheat Straw and phosphate as German basic slag on loss of soil and fertilizer nitrogen was studied. Wheat straw not only conserved soil and fertilizer nitrogen but also helped in nitrogen fixation. A temporary exhaustion of available nitrogen observed with the addition of wheat straw stresses the need of incorporation of organic materials with wider C : N ratio

several weeks before the expected nitrogen need of the plant. German basic slag was also found to be helpful in reducing the loss of nitrogen and increasing nitrogen fixation. Organic materials and phosphate could thus be used for increasing humus reserves of the soil and conserving costly fertilizer nitrogen as well.

References

1. Allison, F. E. *Advanc. Agron.* **7**: 213, 1955.
2. A. O. A. C. Official Methods of Analysis, 8th ed. Washington D. C. 1955.
3. Bartholomew, W. V. and Hiltbold, A. E. *Soil Sci.* **73** : 193, 1952.
4. Bremmer, J. M. and Shaw, K. *J. agric Sci.* **51** : 22, 1958.
5. Chandra, P. and Bollen, W. B. *J. Ind. Soil Sci.* **7** : 115, 1959.
6. Chandra, P., Bollen, W. B. and Harward, M. E. *Proc. West Soc. Soil Sci. (Abst.)* 31, 1957
7. Crowther, C. M. and Yates, F. *Emp. J. Exp. Agric.* **9** : 77, 1941.
8. Dhar, N. R. Presidential Address, *Nat. Acad. Sci. India,* 1955.
9. Dhar, N. R. and Ghosh G. P. *Proc. Nat. Acad. Sci. India,* **25-A** (6) : 1956.
10. Harmsen, G. W. and Vanschrewen, D. A. *Advanc. Agron.* **7** : 299, 1955.
11. Jaiswal, S. P. *D.Phil. Thesis, Allahabad University,* 1964.
12. John, Brooks, R. St. *2nd int. Congr. Microb. London, Report of Proceedings Harrison Sons, London,* 1936.
13. Mc Garity, J. W., Gilmour, C. M. and Bollen, W. B. *Canad. J. Microbiol* **4** : 303, 1959.
14. Mac Vicar, R., Garmann W. L. and Wall, R. *Proc. Soil Sci. Soc. Amer.* **15** : 265, 1951.
15. Piper, C. S. *Soil and Plant analysis, Adelaide,* 1947.
16. Russell, E. J. Soil Conditions and plant growth, *Longmans Green and Co, London,* 1950.
17. Shrikhanade, J. G. *Industr. Engng. Chem. (Anal.)* **13** : 187, 1943.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968

Studies on Nitrogen Fixation with pure culture of Azotobacter containing different energy materials in presence and absence of Di-Calcium phosphate

By

N. R. DHAR *and* R. S. PANWAR

Sheila Dhar Institute of Soil Science, Allahabad University, Allahabad

Our experiment deals with Nonsymbiotic aerobic microorganism *i.e.*, Azotobacter. Experiments were started with pure cultures of Azotobacter using 2·0 gms. carbon as energy materials *viz.*, Mannitol, Starch, Glucose and finely powdered (100 mesh) Wheat straw in presence and absence of $CaHPO_4$ (0·5 gm.). One set was kept exposed and other set covered with black cloth in artificial light (using 200 watt bulb). In each 500 ml. flask, 300 ml. of following nitrogen free medium (Allen's Base Medium 77) for Azotobacter was used.

Dipotassium phosphate (K_2HPO_4)	0·5 gm.
Magnesium sulphate ($MgSO_4.7H_2O$)	0·2 gm.
Sodium chloride (NaCl)	0·2 gm.
Mangenese sulphate ($MnSO_4.4H_2O$)	Trace.
Ferric chloride ($FeCl_3\ 6H_2O$)	Trace.
Distilled water	1000 ml.

The above medium was sterilized at 15 lbs. pressure for about 15 to 20 minutes in an autoclave. Energy materials in presence and absence of $CaHPO_4$ with 300 ml. of medium were sterilized. After sterilization 10 ml. of Azotobacter suspension was added in each 500 ml. flask containing the medium. The experiment's estimation was estimated after a certain interval of time. In Table I, results were obtained after a lapse of 40 days in dark and light in presence and absence of $CaHPO_4$. The results clearly indicate that the oxidation was faster in the covered flasks as compared to the exposed ones after 40 days of exposure with all energy materials with and without phosphate. More nitrogen was fixed in the dark than in the light. But, it is most important to note that the efficiency (mgms. of N fixed per gram of carbon oxidised) was always higher in light than in the dark.

These results clearly indicate when the system is exposed to light for a short interval of time *i.e.*, 40 days, oxidation of carbon in the dark sets may be higer than in the exposed ones. But when the exposure to light is for longer periods (110 days), the oxidation of carbon and fixation of nitrogen is greater in light than in dark as shown in table 2. The amount of Nitrogen fixed in mgms. per gram of carbon oxidised is always greater in light than in the dark in all sets. The sets containing $CaHPO_4$, showed a good amount of nitrogen fixation than its absence. There is marked fixation of nitrogen in sets containing energy materials + Phosphate. 300 ml. Medium + Mannitol (as 2 gms. C) + 0·5 gm. $CaHPO_4$ + 10 ml. of Azotobacter suspension have showed higher efficiency *i.e.*, 19·3 in 40 days interval, in light than the other energy materials used. It was found that the number of Azotobacter cells per 10 ml. was much higher in the dark than in the light in all the sets. Dhar and Ghildyal

TABLE I

Treatments		Initial carbon (gm.)	Total carbon after 40 days (gm.)	Total carbon oxidised after 40 days. (gm.)	Total Nitrogen fixed after 40 days (gm.)	Efficiency	Initial Azotobacter in mille/10 ml. suspension	Azotobacter count in mille/10 ml. suspension after 40 days
1. 300 ml. Medium + 2gms. Carbon as Mannitol + 10 ml. Azotobacter suspension	*Light*	2·0320	1·8898	0·1422	2·49	17·5	1·3	2·4
	Dark	2·0320	1·6475	0·3845	3·92	10·2	1·3	18·1
2. 300 ml. Medium+2 gms. Carbon as Glucose + 10 ml. Azotobactor suspension	*Light*	2·0310	1·8904	0·1406	2·43	17·3	1·2	2·3
	Dark	2·0310	1·6480	0·3830	3·79	9·3	1·2	15·5
3. 300 ml. Medium + 2 gms. Carbon as Starch + 10 ml. Azotobacter suspension	*Light*	2·0350	1·8956	0·1394	2·37	17·0	1·15	2·15
	Dark	2·0350	1·6625	0·3725	3·61	9·7	1·15	14·2
4. 300 ml. Medium + 2 gms. Carbon as Wheat straw + 10 ml. Azotobacter suspension	*Light*	2·0254	1·9221	0·1033	1·55	15·0	1·12	2·0
	Dark	2·0254	1·8206	0·2048	1·70	8·3	1·12	12·2
5. 300 ml. Medium + 2 gms. Carbon as Mannitol + 0·5 gm. $CaHPO_4$ + 10 ml. Azotobacter suspension	*Light*	2·0320	1·8740	0·1580	3·04	19·3	1·3	2·6
	Dark	2·0320	1·6446	0·3874	3·99	10·3	1·3	20·8
6. 300 ml. Medium + 2 gms. Carbon as Glucose+ 0·5 gm. $CaHPO_4$ + 10 ml. Azotobacter suspension	*Light*	2·0310	1·8745	0·1565	2·97	19·0	1·2	2·5
	Dark	2·0310	1·6459	0·3851	3·89	10·1	1·2	20·0
7. 300 ml. Medium + 2 gms. Carbon as Starch+0·5 gm. $CaHPO_4$ +10 ml. Azotobacter suspension	*Light*	2·0350	1·8795	0·1555	2·92	18·7	1·15	2·32
	Dark	2·0350	1·6585	0·3765	3·69	9·8	1·15	16·6
8. 300 ml. Medium + 2 gms. Carbon as Wheat straw+0·5 gm. $CaHPO_4$ + 10 ml. Azotobacter suspension	*Light*	2·0254	1·9217	0·1037	1·68	16·2	1·12	2·28
	Dark	2·0254	1·8158	0·2096	1·74	8·3	1·12	14·0

TABLE 2

Treatments		Initial carbon (gm.)	Total carbon after 110 days (gm.)	Total carbon oxidised after 110 days (gm.)	Total Nitrogen fixed after 110 days (gm.)	Efficiency	Initial Azotobacter in mille/10 ml. suspension	Azotobacter count in mille/10 ml. suspension after 110 days
1. 300 ml. Medium + 2 gms. carbon as Mannitol + 10 ml. Azotobacter suspension	*Light*	2·0320	1·5299	0·5021	6·38	12·7	1·3	3·9
	Dark	2·0320	1·5483	0·4837	4·45	9·2	1·3	39·6
2. 300 ml. Medium + 2 gms. carbon as Glucose + 10 ml. Azotobacter suspension	*Light*	2·0310	1·5324	0·4986	6·23	12·5	1·2	3·72
	Dark	2·0310	1·5550	0·4760	4·38	9·2	1·2	36·8
3. 300 ml. Medium + 2 gms. carbon as Starch + 10 ml. Azotobacter suspension	*Light*	2·0350	1·5378	0·4972	6·07	12·3	1·15	3·25
	Dark	2·0350	1·5647	0·4703	4·28	9·1	1·15	32·7
4. 300 ml. Medium + 2 gms. carbon as Wheat straw + 10 ml. Azotobacter suspension	*Light*	2 0254	1·6467	0·3787	4·32	11·5	1·12	3·6
	Dark	2·0254	1·7215	0·3039	2·31	7·6	1·12	30·1
5. 300 ml. Medium + 2 gms. carbon as Mannitol + 0·5 gm. $CaHPO_4$ + 10 ml. Azotobacter suspension	*Light*	2·0320	1·4117	0·6203	8·37	13·4	1·3	4·2
	Dark	2·0320	1·5460	0·4860	4·52	9·3	1 3	49·0
6. 300 ml. Medium + 2 gms. carbon as Glucose + 0·5 gm. $CaHPO_4$ + 10 ml. Azotobacter suspension	*Light*	2·0310	1·4308	0·6002	7·82	13·3	1·3	3·9
	Dark	2·0310	1·5493	0·4817	4·48	9·3	1·3	45·6
7. 300 ml. Medium + 2 gms. carbon as Starch + 0·5 gm. $CaHPO_4$ + 10 ml. Azotobacter suspension	*Light*	2·0350	1·4374	0·5976	7·66	12·8	1·15	3·2
	Dark	2·0350	1·5600	0·4750	4·37	9·2	1·15	39·8
8. 300 ml. Medium + 2 gms. carbon as Wheat straw + 0·5 gm. $CaHPO_4$ + 10 ml. Azotobacter suspension	*Light*	2·0254	1·6393	0·3861	4·75	12·3	1·12	3·0
	Dark	2·0254	1·7189	0·3065	2·36	7·7	1·12	35·5

(1950) had observed similar abundant growth of Azotobacter in the dark, and in light, the growth was adversely affected presumably due to light radiation.

Dhar and Seshacharyulu (1941) also observed that the fixation of 11·75 mgms. nitrogen in the light and 18·5 mgms. in the dark in 100 ml. of tap water containing 2 gms. Mannitol, 0·02 gm. K_2HPO_4 and 1 gm. $CaCO_3$ containing pure culture of Azotobacter after 63 days of exposure to sunlight. Dhar and Ghildyal (1950) showed 8·5 mgm. of Nitrogen fixed in the dark as against 4·25 mgm. fixed in light Dhar and Sohan Lal (1967) also reported the fixation of 2·22 mgms. nitrogen in light (artificial) and 3·84 mgms. in the dark. But as the exposure is increased the difference between the carbon oxidation in light and dark becomes less. Uppal, Patel and Dagi (34) have shown that Azotobacter plays an important role in nitrogen recuperate of rice soils at Rajkot (India).

It seems therefore that when the exposure is less, bacterial activity predominates but more economy is exercised by photochemical reaction as the 'efficiency' is always high in light than in the dark. As the exposure increases, the photochemical action also gradually increases and finally predominates. Azotobacter numbers are always greater in dark sets than the light sets.

This shows that photochemical reactions are more efficient and economical as per gram of carbon oxidised in light, more nitrogen is fixed. It is clear, therefore, that the efficiency of nitrogen fixation in light in presence of $CaHPO_4$, with pure culture of Azotobacter fed with energy material is always greater in light. Phosphate (0·5 gm. $CaHPO_4$) with energy materials 2 gms. carbon as Mannitol in presence of 300 ml. medium and Azotobacter suspension (10 ml.) showed maximum nitrogen fixation in light in 110 days interval of time. The nitrogen fixation efficiency of energy materials are as follows :—

Mannitol > Glucose > Starch > Wheat straw.

Summary

Nitrogen fixing capacity of different energy materials like glucose, mannitol, wheat straw and starch in combination with Azotobacter and Di-calcium phosphate was investigated.

Azotobacter cultures containing these materials were exposed to light and dark separately. It has been found that when these energy materials undergo slow oxidation they fix nitrogen. In each case fixation is more in light than in dark. Azotobacter number decreases in light and increases in dark.

In all sets results are better in presence of Di-calcium phosphate than in its absence. The nitrogen fixing efficiency of energy materials in presence and absence of phosphate is as follows :—

Mannitol > Glucose > Starch > Wheat Straw.

References

Dhar, N. R. and Seshacharyulu, E. V. *Proc. Nat. Acad. Sci. Ind.* **11** : 97, 1941.

Uppal, Patel and Dagi, **34** :

Dhar, N. R. and Ghildyal, B. N. P. *D.Phil thesis, Univ. Allahabad,* 1950.

Proceeding of the symposium on Radioisotopes, Fertilizer and Cowdung Gas plant December, 1959, I. C. A. R.

Dhar, N. R. and Sohan Lal. *D.Phill thesis, Univ. Allahabad,* 1967.

Proc Nat. Acad. Sci., India, 38(A), I & II, 1968.

Decomposition of Basic Slags by Water

By

N. R. DHAR *and* B. S. GUPTA

Sheila Dhar Institute, University of Allahabad, Allahabad

Basic slag, a bye product of Steel Industries, is the mixture of silico-carnotite, steadite, thomasite and hilgenstockite[1] and oxides of several trace elements. The composition of the basic slag depends upon the nature and composition of raw materials of Steel Plants. India—a poor country—produces very low grade basic slag while the European countries produce high grade basic slags in respect of phosphorus content. Generally, European basic slags are used as a fertilizer, but the utilization of Indian basic slags has to be taken up and hence further investigation is needed. In this paper, the authors have described their studies on the effect of water on high and low grade basic slags, obtained from Germany, Belgium and different steel industries in India.

Experimental

Four grams of each basic slag (100 mesh sieved) were taken into a 500 ml. conical flask and 400 ml. of conductivity water were added to it. The conical flasks were kept at 30°C in a thermostat maintained at 30°-0·5°C for a period of 300 days. The electrical conductivity pH, CaO and P_2O_5 were determine with lapse of time, as recorded in tables, by frequent shaking by hands for half an hour daily before filtration. Electrical conductivity was determined with the help of the instrument known as Kohlransch Slide wire Cat. No. 4258, Leeds and Northrup, Philadelphia, U. S. A. The pH of all solutions were measured by the Beckman Glass Electrode, pH Meter, Model H-2, manufactured by Beckman Instrument INC. California, U.S.A. Other estimations were carried out by the help of[2 to 5].

Discussion

From a close study of the foregoing results, the influence of time on the decomposition of slags in water, pH and electrical conductivity of saturated solution of different basic slags becomes evident. In general, all basic slags liberate appreciable amounts of P_2O_5 in solution. The pH and electrical conductivity increase with lapse of time upto 60 days. The increase in pH can be explained from the view point that more lime and other basic materials go into solution than P_2O_5 or acidic materials. Moreover, due to the presence of basic materials—chiefly $Ca(OH)_2$ in the solution, the hydrolysis of calcium phosphates present in basic slags, is retarded to a great extent. It has been observed that the sp. conductivity increases to a maximum from 40 to 60 days and afterwards decreases slowly or remain constant. The amounts of CaO and P_2O_5 also slightly decrease with increasing time after 80 days. This may be due to formation of a precipitate of basic calcium phosphate. This view is further supported by the fact that in the case of German and Belgium basic slags, the decrease in conductivity is greater than in the other cases. The smaller amounts of P_2O_5 form smaller quantities of basic phosphates in course of time. The pH measurements and the amount of P_2O_5 are also agreement with this conclusion.

TABLE I

Analysis of different basic slags

Symbols	Tata basic slag	Kulti basic slag	Durgapur basic slag	Rourkela basic slag	German basic slag	Belgium basic slag
SiO_2 etc.	15·6846	16·9677	20·1640	22·4600	11·4665	11·9867
Iron (Total)	10·8265	9·8100	12·1884	11·5966	9·1263	10·0216
Fe_2O_3	3·8000	4·1000	5·2900	5·6466	4·1233	4·9888
FeO	10·4678	8·9000	10·8764	9·8000	7·9999	8·3688
Al_2O_3	5·4320	6·4860	6·8748	6·3646	3·0678	2·9646
CaO	38·6946	40·1800	37·7785	40·0000	42·3467	41·6846
MnO	2·9079	2·9978	4·6633	3·1674	4·8736	4·1844
MgO	4·8486	4·1346	5·6726	6·0174	4·9800	4·6788
K_2O	0·6474	0·3364	0·5644	Traces	Traces	Traces
Halides	0·1768	0·1967	0·2233	0·1884	0·1067	0·0988
Sulphur	0·3674	0·4678	0·6078	0·6446	0·2222	0·2567
V_2O_5	0·4881	0·4136	0·3468	0·3394	0·6438	0·5488
Cr_2O_2	0·3973	0·3688	0·2988	0·2767	0·4678	0·3999
TiO_2	0·3126	0·2566	0·2333	0·2188	0·4784	0·2999
CuO	0·0053	0·0044	0·0044	0·0038	0·0048	0·0088
ZnO	0·0064	0·0056	0·0086	0·0047	0·0056	0·0060
MoO_3	0·0080	0·0088	0·0100	0·0093	0·0108	0·0102
P_2O_5 (Total)	7·7380	4·1680	3·4868	2·0684	17·8683	16·6640
P_2O_5 (Available)	4·1020	2·0340	1·4802	0·8644	7·9672	7·6360
Sp. conductivity in mhos $X10^{-4}$	3·14	4·18	3·76	3·98	6·82	6·72
pH	9·50	9·70	9·15	9·65	8·85	8·75

TABLE 2

Solubility of Tata Basic Slag in Water

Period in hours or days	Sp. Conductivity in Mhos X10^{-4}	pH of the solution	Phosphorus as P_2O_5 in gms/litre	Calcium as CaO in gms/litre
0	—	7·00	—	—
0·25 hrs.	2·48	8·85	0·00567	0·05304
0·50 ,,	2·63	8·95	0·00624	0·05789
0·75 ,,	2·78	9·05	0·00667	0·06178
1·00 hr.	2·82	9·10	0·00684	0·06364
1·50 hrs.	2·86	9·15	0·00686	0·06380
2·00 ,,	2·87	9·15	0·00688	0·06382
3·00 ,,	2·88	9·20	0·00692	0·06386
4·00 ,,	2·90	9·20	0·00694	0·06389
6·00 ,,	2·92	9·25	0·00696	0·06393
8·00 ,,	2·94	9·25	0·00704	0·06396
10·0 ,,	2·96	9·30	0·00708	0·06400
16·0 ,,	3·06	9·45	0·00715	0·06413
24·0 ,,	3·14	9·50	0·00720	0·06420
36·0 ,,	3·36	9·55	0·00724	0·06430
2 days	3·52	9·55	0·00730	0·06438
3 ,,	3·64	9·60	0·00732	0·06447
4 ,,	3·71	9·65	0·00733	0·06452
5 ,,	3·75	9·65	0·00733	0·06454
10 ,,	3·88	9·75	0·00736	0·06467
15 ,,	3·97	9·80	0·00738	0·06478
20 ,,	4·12	9·80	0·00740	0·06484
30 ,,	4·46	9·85	0·00743	0·06497
40 ,,	4·68	9·85	0·00745	0·06500
60 ,,	4·70	9·90	0·00748	0·06532
80 ,,	4·66	9·85	0·00748	0·06528
100 ,,	4·60	9·75	0·00745	0·06500
200 ,,	4·33	9·70	0·00740	0·06468
300 ,,	4·20	9·70	0·00736	0·06462

TABLE 3

Solubility of Kulti Basic Slag in Water

Period in hours or days	Sp. Conductivity in Mhos $X10^{-4}$	pH of the solution	Phosphorus as P_2O_5 in gms/litre	Calcium as CaO in gms/litre
0	—	7·00	—	—
0·25 hrs.	3·18	8·95	0·00316	0·06164
0·50 ,,	3·48	9·10	0·00340	0·06674
0·75 ,,	3·64	9·15	0·00368	0·06996
1·00 hr.	3·86	9·15	0·00388	0·07286
1·50 hrs.	3·89	9·20	0·00390	0·07299
2·00 ,,	3·99	9·25	0·00392	0·07312
3·00 ,,	3·92	9·35	0·00396	0·07344
4·00 ,,	3·96	9·40	0·00399	0·07360
6·00 ,,	3·98	9·45	0·00406	0·07373
8·00 s,	4·00	9·55	0·00417	0·07384
10·0 ,,	4·08	9·55	0·00422	0·07391
16·0 ,,	4·13	9·65	0·00429	0·07413
24·0 ,,	4·18	9·70	0·00433	0·07423
36·0 ,,	4·22	9·75	0·00436	0·07436
2 days	4·26	9·80	0·00437	0·07436
3 ,,	4·28	9·85	0·00440	0·07442
4 ,,	4·29	9·85	0·00442	0·07447
5 ,,	4·30	4·30	0·00443	0·07450
10 ,,	4·46	9·95	0·00446	0·07462
15 ,,	4·57	9·95	0·00448	0·07470
20 ,,	4·64	10·05	0·00450	0·07476
30 ,,	4·98	10·10	0·00453	0·07483
40 ,,	5·12	10·10	0·00455	0·07490
60 ,,	5·16	10·20	0·00457	0·07500
80 ,,	5·08	10·15	0·00458	0·07503
100 ,,	4·96	10·05	0·00456	0·07492
200 ,,	4·76	10·00	0·00452	0·07480
300 ,,	4·66	9·90	0·00450	0·07468

TABLE 4

Solubility of Durgapur Basic Slag in Water

Period in hours or days	Sp. Conductivity in Mhos $X10^{-1}$	pH of the solution	Phosphorus as P_2O_5 in gms/litre	Calcium as CaO in gms/litre
0	—	7·00	—	—
0·25 hrs.	3·23	8·75	0·00258	0·06329
0·50 ,,	3·30	8·75	0·20267	0·06374
0·75 ,,	3·32	8·80	0·00272	0·06456
1·00 hr.	3·34	8·85	0·00276	0·06484
1·50 hrs.	3·37	8·90	0·00279	0·06500
2·00 ,,	3·41	8·95	0·00283	0·06538
3·00 ,,	3·43	9·00	0·00294	0·06597
4·00 ,,	3·45	9·00	0·00303	0·06664
6·00 ,,	3·50	9·05	0·00319	0·06736
8·00 ,,	3·56	9·05	0·00338	0·06826
10·0 ,,	3·59	9·10	0·00356	0·06908
16·0 ,,	3·64	9·10	0·00370	0·06982
24·0 ,,	3·76	9·15	0·00382	0·07002
36·0 ,,	3·87	9·20	0·00396	0·07036
2 days	3·94	9·20	0·00399	0·07068
3 ,,	4·06	9·25	0·00410	0·07116
4 ,,	4·13	9·30	0·00413	0·07134
5 ,,	4·21	9·30	0·00415	0·07158
10 ,,	4·38	9·40	0·00420	0·07192
15 ,,	4·49	9·45	0·00423	0·07234
20 ,,	4·56	9·45	0·00425	0·07235
30 ,,	4·67	9·55	0·00427	0·07294
40 ,,	4·74	9·60	0·00428	0·07330
60 ,,	4·80	9·60	0·00429	0·07346
80 ,,	4·95	9·55	0·00429	0·07339
100 ,,	5·20	9·50	0·00428	0·07336
200 ,,	5·25	9·30	0·00424	0·07322
300 ,,	5·00	9·20	0·00418	0·07312

TABLE 3

Solubility of Kulti Basic Slag in Water

Period in hours or days	Sp. Conductivity in Mhos X10^{-4}	pH of the solution	Phosphorus as P_2O_5 in gms/litre	Calcium as CaO in gms/litre
0	—	7·00	—	—
0·25 hrs.	3·18	8·95	0·00316	0·06164
0·50 ,,	3·48	9·10	0·00340	0·06674
0·75 ,,	3·64	9·15	0·00368	0·06996
1·00 hr.	3·86	9·15	0·00388	0·07286
1·50 hrs.	3·89	9·20	0·00390	0·07299
2·00 ,,	3·99	9·25	0·00392	0·07312
3·00 ,,	3·92	9·35	0·00396	0·07344
4·00 ,,	3·96	9·40	0·00399	0·07360
6·00 ,,	3·98	9·45	0·00406	0·07373
8·00 s,	4·00	9·55	0·00417	0·07384
10·0 ,,	4·08	9·55	0·00422	0·07391
16·0 ,,	4·13	9·65	0·00429	0·07413
24·0 ,,	4·18	9·70	0·00433	0·07423
36·0 ,,	4·22	9·75	0·00436	0·07436
2 days	4·26	9·80	0·00437	0·07436
3 ,,	4·28	9·85	0·00440	0·07442
4 ,,	4·29	9·85	0·00442	0·07447
5 ,,	4·30	4·30	0·00443	0·07450
10 ,,	4·46	9·95	0·00446	0·07462
15 ,,	4·57	9·95	0·00448	0·07470
20 ,,	4·64	10·05	0·00450	0·07476
30 ,,	4·98	10·10	0·00453	0·07483
40 ,,	5·12	10·10	0·00455	0·07490
60 ,,	5·16	10·20	0·00457	0·07500
80 ,,	5·08	10·15	0·00458	0·07503
100 ,,	4·96	10·05	0·00456	0·07492
200 ,,	4·76	10·00	0·00452	0·07480
300 ,,	4·66	9·90	0·00450	0·07468

TABLE 4

Solubility of Durgapur Basic Slag in Water

Period in hours or days	Sp. Conductivity in Mhos $X10^{-1}$	pH of the solution	Phosphorus as P_2O_5 in gms/litre	Calcium as CaO in gms/litre
0	—	7·00	—	—
0·25 hrs.	3·23	8·75	0·00258	0·06329
0·50 ,,	3·30	8·75	0·20267	0·06374
0·75 ,,	3·32	8·80	0·00272	0·06456
1·00 hr.	3·34	8·85	0·00276	0·06484
1·50 hrs.	3·37	8·90	0·00279	0·06500
2·00 ,,	3·41	8·95	0·00283	0·06538
3·00 ,,	3·43	9·00	0·00294	0·06597
4·00 ,,	3·45	9·00	0·00303	0·06664
6·00 ,,	3·50	9·05	0·00319	0·06736
8·00 ,,	3·56	9·05	0·00338	0·06826
10·0 ,,	3·59	9·10	0·00356	0·06908
16·0 ,,	3·64	9·10	0·00370	0·06982
24·0 ,,	3·76	9·15	0·00382	0·07002
36·0 ,,	3·87	9·20	0·00396	0·07036
2 days	3·94	9·20	0·00399	0·07068
3 ,,	4·06	9·25	0·00410	0·07116
4 ,,	4·13	9·30	0·00413	0·07134
5 ,,	4·21	9·30	0·00415	0·07158
10 ,,	4·38	9·40	0·00420	0·07192
15 ,,	4·49	9·45	0·00423	0·07234
20 ,,	4·56	9·45	0·00425	0·07235
30 ,,	4·67	9·55	0·00427	0·07294
40 ,,	4·74	9·60	0·00428	0·07330
60 ,,	4·80	9·60	0·00429	0·07346
80 ,,	4·95	9·55	0·00429	0·07339
100 ,,	5·20	9·50	0·00428	0·07336
200 ,,	5·25	9·30	0·00424	0·07322
300 ,,	5·00	9·20	0·00418	0·07312

TABLE 5

Solubility of Rourkela Basic Slag in Water

Period in hours or days	Sp. Conductivity in Mhos X10^{-4}	pH of the solution	Phosphorus as P_2O_5 in gms/litre	Calcium as CaO in gms/litre
0	—	7·00	—	—
0·25 hrs.	2·86	9·00	0·00222	0·06284
0·50 ,,	3·06	9·15	0·00228	0·06362
0·75 ,,	3·19	9·20	0·00231	0·06426
1·00 hr.	3·26	9·20	0·00233	0·06478
1·50 hrs.	3·38	9·25	0·00236	0·06539
2·00 ,,	3·47	9·25	0·00242	0·06586
3·00 ,,	3·66	9·30	0·00248	0·06637
4·00 ,,	3·79	9·35	0·00253	0·06674
6·00 ,,	3·88	9·45	0·00262	0·06726
8·00 ,,	3·90	9·50	0 00269	0·06762
10·0 ,,	3·91	9·50	0·00273	0·06784
16·0 ,,	3·94	9·55	0·00279	0·06817
24·0 ,,	3·98	9·65	0·00284	0·06843
36·0 ,,	4·07	9·70	0·00287	0 06872
2 days	4·12	9·75	0·00288	0·06894
3 ,,	4·15	9·80	0·00290	0·06908
4 ,,	4·22	9·80	0·00292	0·06923
5 ,,	4·27	9·85	0·00292	0·06938
10 ,,	4·30	9·90	0·00295	0·06972
15 ,,	4·33	9·95	0·00298	0·06993
20 ,,	4·35	10·00	0·00300	0·07020
30 ,,	4·38	10·00	0·00303	0·07084
40 ,,	4·40	10·05	0·00305	0·07100
60 ,,	4·40	10·05	0·00307	0·07113
80 ,,	4·36	10·00	0·00305	0·07106
100 ,,	4·27	10·00	0·00302	0·07088
200 ,,	4·19	9·95	0·00300	0·07066
300 ,,	4·16	9·90	0·00292	0·07027

TABLE 6

Solubility of German Basic Slag in Water

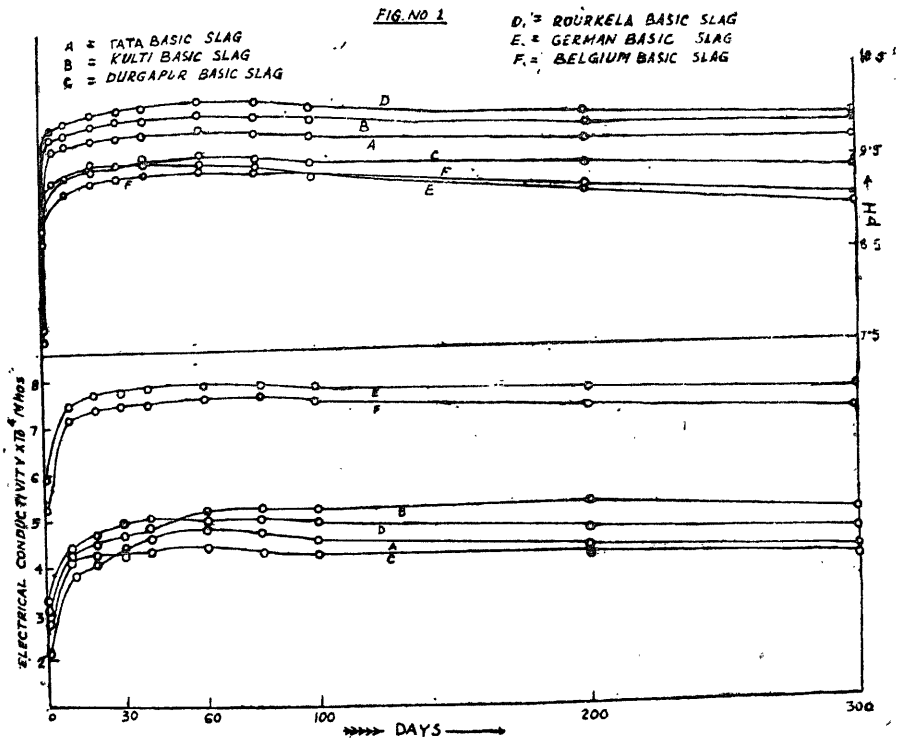
Period in hours or days	Sp. Conductivity in Mhos X10^{-4}	pH of the solution	Phosphorus as P_2O_5 in gms/litre	Calcium as CaO in gms/litre
0	—	7·00	—	—
0·25 hrs.	5·94	7·70	0·00983	0·07236
0·50 ,,	6·06	7·75	0·00999	0·07346
0·75 ,,	6·13	7·75	0·01215	0·07415
1·00 hr.	6·18	7·85	0·01267	0·07486
1·50 hrs.	6·20	7·95	0·01284	0·07544
2·00 ,,	6·28	8·00	0·01296	0·07584
3·00 ,,	6·35	8·10	0·01300	0·07609
4·00 ,,	6·41	8·15	0·01303	0·07653
6·00 ,,	6·50	8·25	0·01307	0·07694
8·00 ,,	6·57	8·30	0·01311	0·07723
10·0 ,,	6·62	8·45	0·01313	0·07768
16·0 ,,	6·70	8·65	0·01319	0·07894
24·0 ,,	6·82	8·85	0·01324	0·07982
36·0 ,,	6·95	8·95	0·01329	0·07999
2 days	7·06	9·00	0·01333	0·08064
3 ,,	7·19	9·05	0·01338	0·08133
4 ,,	7·33	9·05	0·01341	0·08164
5 ,,	7·42	9·10	0·01343	0·08210
10 ,,	7·56	9·20	0·01352	0·08298
15 ,,	7·66	9·25	0·01358	0·08346
20 ,,	7·70	9·25	0·01363	0·08382
30 ,,	7·76	9·30	0·01371	0·08416
40 ,,	7·80	9·30	0·01378	0·08437
60 ,,	7·82	9·35	0·01381	0·08443
80 ,,	7·80	9·25	0·01378	0·08416
100 ,,	7·75	9·20	0·01372	0·08400
200 ,,	7·60	9·10	0·01358	0·08381
300 ,,	7·52	8·95	0·01329	0·08326

TABLE 7

Solubility of Belgium Basic Slag in Water

Period in hours or days	Sp. Conductivity in Mhos X10^{-4}	pH of the solution	Phosphorus as P_2O_5 in gms/litre	Calcium as CaO in gms/litre
0	—	7·00	—	—
0·25 hrs.	5·36	7·60	0·00979	0·07124
0·50 ,,	5·64	7·65	0·00992	0·07156
0·75 ,,	5·80	7·75	0·01213	0·07200
1·00 hr.	5·96	7·85	0·01216	0·07234
1·50 hrs.	6·12	7·90	0·01218	0·07258
2·00 ,,	6·23	8·00	0·01220	0·07280
3·00 ,,	6·33	8·15	0·01227	0·07368
4·00 ,,	6·39	8·25	0·01227	0·07394
6·00 ,,	6·46	8·40	0·01234	0·07417
8·00 ,,	6·51	8·45	0·01246	0·07433
10·0 ,,	6·55	8·50	0·01250	0·07459
16·0 ,,	6·65	8·65	0·01275	0·07473
24·0 ,,	6·72	8·75	0·01280	0·07484
36·0 ,,	6·90	8 80	0·01288	0·07496
2 days	6·96	8·80	0·01292	0·07510
3 ,,	6·99	8·90	0·01298	0·07538
4 ,,	7·03	8·95	0·01303	0·07544
5 ,,	7·08	8·95	0·01305	0·07556
10 ,,	7·26	9 05	0·01314	0·07586
15 ,,	7·39	9 10	0·01323	0·07599
20 ,,	7·45	9·15	0·01330	0·07612
30 ,,	7·54	9·20	0·01340	0·07632
40 ,,	7·60	9·25	0·01345	0·07660
60 ,,	7·64	9·30	0·01348	0·07699
80 ,,	7·61	9·25	0·01345	0·07674
100 ,,	7·57	9·15	0·01340	0·07628
200 ,,	7·44	9·05	0·01326	0·07590
300 ,,	7·33	8·90	0·01306	0·07555

Comparing the solubilities of different basic slags as recorded in tables 1 to 6 and also in fig. No. 1, it can be concluded that the difficulty available phosphates in Indian basic slags are also moderate suppliers of phosphate together with other important elements for the growth of plants and in which decomposition of basic slags by water plays a prominent part. From this experiment it has been proved that the process of hydrolysis of basic slags continues for long periods and behaviour of different basic slags is complex due to the complexity of their constitutions. The residual value of phosphates in agriculture observed by Scarseth & Chandler[6] Volk[7], Ensminger and Cope[8] may be explained from the view point of the phenomenon of hydrolysis.



It appears from the chemical analysis of basic slags as shown in table number one that CaO and MgO contents vary from 38% to 42% and 4% to 9% respectively. In other words, these basic oxides are present in these basic slags in more or less in equal amounts. Similarly the total iron varies from 9% to 12% showing comparatively small variation. MnO_2 varies from 3% to 5%. On the other hand, in German basic slag and Belgium basic slag, the silica content varies only 11% to 12%, but in the four Indian basic slags the amounts of silica are 15·7% to 22·4% Similarly the amounts of phosphorus greatly vary from 18% to 2·8%. The indication is that the smaller the amount of phosphorus, the greater the content of silica in basic slags. Therefore, Indian basic slags are richer in silicates than European basic slags which are rich in phosphorus. Wagner[9] reported that the silica helps in the availability of phosphorus and other materials to the plants.

Recently Dhar and coworkers[10] have largely utilized Indian basic slags in agriculture specially by mixing with waste organic matter. The Indian basic slags have been found to be profitable in crop production.

Summary

The decomposition of Tata, Kulti, Durgapur, Rourkela, German and Belgium Basic Slags by water has been studied and it has been observed that all basic slags decompose considerably simply by keeping them in contact with water at room temperature. It is also observed that during the decomposition of basic slags, basic calcium phosphate is formed with lapse of time. This is an hydrolysis phenomenon.

References

1. Kroll, V. A. *J. Iron Steel Inst., England,* **2** : 126, 1911.
2. Washington, H. S. The Chemical Analysis of Rocks. *John Wiley and Sons, Inc.,* 4th Ed., 1930.
3. Hillebrand, W. F. and Lundell, G. E. F. Applied Inorganic Analysis. *John Wiley and Sons, Inc.,* 1955.
4. Scott, Wilered W. Standard Methods of Chemical Analysis. *Longmans Green and Co.,* 2nd Ed., 1946.
5. Snell and Snell. Colorimetric Methods of Analysis. *D. Van Norstrand and Co.,* Vol **1** : 1958.
6. Scarseth, G. D. and Chandler, W. V. *J. Am. Soc. Agron.,* **30** : 361-374, 1938.
7. Volk, G. W. *Ibid.,* **37** : 330-340, 1945.
8. Ensminger, L. E. and Cope, J. T. *Ibid.,* **39** : 1-11, 1947.
9. Wagner, P. *Dungungsfragen,* **1** : 28, 1896.
10. Dhar, N. R. *Proc. Nat. Acad. Sci., India,* **21** : 156, 1952 ; *Indian Agriculturist,* **3** : 1959 ; *Presidential Address (Roorkee), India,* 1961 ; *Proc. Nat. Acad. Sci.,* **33** : 357-78, 1963.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968

Effect of Bacteria and Algae separately as well as in their association in light on Nitrogen Fixation in a composite medium containing Glucose

By

N. R. DHAR, S. LAL *and* R. S. PANWAR

Sheila Dhar Institute of Soil Science, Allahabad University, Allahabad

For the experiment, a composite medium containing all the nutrients needed for Azotobacter, Rhizobium and Algae, was utilized. All the ingredients were weighed separately for Azotobacter, Rhizobium, Tolypothrix, Anabaena and Chlorella media. The following ingredients were used for different media.

Medium for Azotobacter		Medium for Rhizobia		Medium for chlorella, Anabaena and Tolypothrix	
1. K_2HPO_4	0·5 gm.	K_2HPO_4	0·5 gm.	K_2HPO_4	0·2 gm.
2. $MgSO_4.7H_2O$	0·2 gm.	$MgSO_4.7H_2O$	0·2 gm.	$MgSO_4.7H_2O$	0·2 gm.
3. NaCl	0·2 gm.	NaCl	0·1 gm.		
4. $MnSO_4.4H_2O$	trace	$CaCO_3$	3·0 gm.	$CaCl_2$	0·1 gm.
5. $FeCl_3.6H_2O$	trace	Mannitol	10 gm.	$FeCl_3$ (1%)	2 drops.
		Yeast extract	100 ml.	Distilled water	1000 ml.
6. Distilled water	1000 ml.	Distilled water	900 ml.	Minus nitrogen source.	

Then all the media were mixed into make a composite medium. 300 ml. of this composite medium was taken in each 500 ml. flask. After adding 1 gm. Carbon as glucose (as energy source) in each flask containing enriched medium, all the flasks were sterilized in an autoclave for 45 minutes at 15 lbs. pressure. In this sterile medium, bacteria and algae were carefully inoculated. Then these flasks were arranged on the table side by side and two feet below a 100 watt electric bulb.

Inoculation technique : 10 ml. of suspension prepared from stock culture of each Azotobacter and Rhizobium prepared in sterile water blanks, were transfered into the system with a sterile micropipette to the enriched medium.

The algal cultures were plated in agar medium wherein algal material was allowed to grow. From a healthy growth, equal quantity of algal growth was cut with the help of inoculum cutter and transferred to the enriched medium.

The cultures were incubated at room temperatures and the contents of all flasks were analysed after some interval of time. The results obtained are presented in the following tables :

TABLE 1

Treatments	Initial carbon (gm.)	After 60 days (In light) Total carbon (gm.)	Total nitrogen (gm.)	Nitrogen fixed (mgm.)
1. Control (300 ml. medium+1·0 gm. Carbon as Glucose).	1·2102	1·0802	0·00232	2·32
2. 300 ml. medium+1 gm. C as Glucose +Azotobacter.	1·2102	1·1711	0·00237	2·37
3. 300 ml. medium+1 gm. C as Glucose +Rhizobium.	1·2102	1·1699	0·00248	2·48
4. 300 ml. medium+1 gm. C as Glucose +Azotobacter+Rhizobium.	1·2102	1·1895	0·00287	2·87
5. 300 ml. medium+1 gm. C as Glucose +Chlorella.		No Growth.		
6. 300 ml. medium+1 gm. C as Glucose +Chlorella+Azotobacter.	1·2102	1·1887	0·00238	2·38
7. 300 ml. medium+1 gm. C as Glucose +Chlorella+Rhizobium.	1·2102	1·2027	0·00252	2·52
8. 300 ml. medium+C as Glucose + Chlorella + Azotobacter + Rhizobium.	1·2102	1·2043	0·00254	2·54
9. 300 ml. medium+1 gm. C as Glucose +Anabaena.	1·2102	1·2175	0·00258	2·58
10. 300 ml. medium+1 gm. C as Glucose +Anabaena+Azotobacter.	1·2102	1·2180	0·00266	2·66
11. 300 ml. medium+1 gm. C as Glucose +Anabaena+Rhizobium.	1·2102	1·2187	0·00270	2·70
12. 300 ml. medium+1 gm. C as Glucose +Anabaena+Azotobacter+ Rhizobium.	1·2102	1·2174	0·00273	2·73
13. 300 ml. medium+1 gm. C as Glucose +Tolypothrix.	1·2102	1·2185	0·00330	3·20
14. 300 ml. medium+1 gm. C as Glucose +Tolypothrix+Azotobacter.	1·2102	1·2189	0·00332	3·32
15. 300 ml. medium+1 gm. C as Glucose +Tolypothrix+Rhizobium.	1·2102	1·2200	0·00335	3·35
16. 300 ml. medium+1 gm. C as Glucose +Tolypothrix+Azotobacter +Rhizobium.	1·2102	1·2201	0·00338	3·38
17. 300 ml. medium+1 gm. C as Glucose +Chlorella+Anabaena.	1·2102	1·2173	0·00239	2·39
18. 300 ml. medium+1 gm. C as Glucose +Chlorella + Anabaena + Azotobacter.	1·2102	1·2184	0·00266	2·66

Treatments	Initial carbon (gm.)	Total carbon (gm.)	Total nitrogen (gm.)	Nitrogen fixed (mgm.)
19. 300 ml. medium+1 gm. C as Glucose + Chlorella + Anabaena + Rhizobium.	1·2102	1·2190	0·00271	2·71
20. 300 ml. medium+1 gm. C as Glucose +Anabaena+Azotobacter+Rhizobium.	1·2102	1·2192	0·00273	2·73
21. 300 ml. medium+1 gm. C as Glucose +Chlorella+Tolypothrix.	1·2102	1·2187	0·00336	3·26
22. 300 ml. medium+1 gm. C as Glucose +Chlorella+Tolypothrix + Azotobacter.	1·2102	1·2187	0·00342	3·42
23. 300 ml. medium+1 gm. C as Glucose +Chlorella+Tolypothrix + Rhizobium.	1·2102	1·2206	0·00346	3·46
24. 300 ml. medium+1 gm. C as Glucose +Chlorella+Tolypothrix + Azotobacter+Rhizobium.	1·2102	1·2204	0·00348	3·48
25. 300 ml. medium+1 gm. C as Glucose +Anabaena+Tolypothrix.	1·2102	1·2202	0·00343	3·43
26. 300 ml. medium+1 gm. C as Glucose +Anabaena+Tolypothrix + Azotobacter.	1·2102	1·2203	0·00338	3·38
27. 300 ml. medium+1 gm. C as Glucose +Anabaena+Tolypothrix +Rhizobium.	1·2102	1·2205	0·00333	3·33
28. 300 ml. medium+1 gm. C as Glucose +Anabaena+Tolypothrix+Azotobacter+Rhizobium.	1·2102	1·2205	0·00351	3·51
29. 300 ml. medium+1 gm. C as Glucose + Chlorella + Anabaena + Tolypothrix.	1·2102	1·2214	0·00346	3·46
30. 300 ml. medium+1 gm. C as Glucose + Chlorella + Anabaena + Tolypothrix+Azotobacter.	1·2102	1·2202	0·00335	3·35
31. 300 ml. medium+1 gm. C as Glucose + Chlorella + Anabaena + Tolypothrix+Rhizobium.	1·2102	1·2208	0·00338	3·38
32. 300 ml. medium+1 gm. C as Glucose + Chlorella + Anabaena + Tolypothrix+Azotobacter+Rhizobium.	1·2102	1·2211	0·00356	3·56

TABLE 2

After 170 days (In light)

Treatments	Initial carbon (gm.)	Total carbon (gm.)	Total nitrogen (gm.)	Nitrogen fixed (mgm.)
1. Control (300 ml. Nutrients composite media+1 gm. C as Glucose.	1·2102	0·8592	0·00310	3·10
2. 300 ml. medium+1 gm. C as Glucose +Azotobacter.	1·2102	1·0538	0·00292	2·92
3. 300 ml. medium+1 gm. C as Glucose +Rhizobium.	1·2102	1·0229	0·00297	2·97
4. 300 ml. medium+1 gm. C as Glucose +Azotobacter+Rhizobium.	1·2102	1·1139	0·00334	3·34
5. 300 ml. medium+1 gm. C as Glucose +Chlorella.		No growth		
6. 300 ml. medium+1 gm. C as Glucose +Chlorella+Azotobacter.	1·2102	1·1130	0·00288	2·88
7. 300 ml. medium+1 gm. C as Glucose +Chlorella+Rhizobium.	1·2102	1·1735	0·00300	3·00
8. 300 ml. medium+1 gm. C as Glucose +Chlorella+Azotobacter +Rhizobium.	1·2102	1·1645	0·00301	3·01
9. 300 ml. medium+1 gm. C as Glucose +Anabaena.	1·2102	1·2168	0·00314	3·14
10. 300 ml. medium+1 gm. C as Glucose +Anabaena+Azotobacter.	1·2102	1·2170	0·00315	3·15
11. 300 ml. medium+1 gm. C as Glucose +Anabaena+Rhizobium.	1·2102	1·2180	0·00323	3·23
12. 300 ml. medium+1 gm. C as Glucose +Anabaena+Azotobacter+Rhizobium.	1·2102	1·2190	0·00326	3·26
13. 300 ml. medium+1 gm. C as Glucose +Tolypothrix.	1·2102	1·2173	0·00371	3·71
14. 300 ml. medium+1 gm. C as Glucose +Tolypothrix+Azatobacter.	1·2012	1·2184	0·00369	3·69
15. 300 ml. medium+1 gm. C as Glucose +Tolypothrix+Rhizobium.	1·2102	1·2192	0·00370	3·70
16. 300 ml. medium+1 gm. C as Glucose + Tolypothrix + Azotobacter + Rhizobium.	1·2102	1·2191	0·00380	3·80
17. 300 ml medium+1 gm. C as Glucose +Chlorella+Anabaena.	1·2102	1·2167	0·00279	2·79
18. 300 ml. medium+1 gm. C as Glucose + Chlorella + Anabaena + Azotobacter.	1·2102	1·2180	0·00281	2·81

Treatments	Initial carbon (gm.)	Total carbon (gm.)	Total nitrogen (gm.)	Nitrogen fixed (mgm.)
19. 300 ml. medium+1 gm. C as Glucose +Chlorella + Anabaena + Rhizobium.	1·2102	1·2190	0·00283	2·83
20. 300 ml. medium+1 gm. C as Glucose + Chlorella + Anabaena + Azotobacter + Rhizobium.	1·2102	1·2190	0·00311	3·11
21. 300 ml. medium+1 gm. C as Glucose +Chlorella+Tolypothrix.	1·2102	1·2168	0·00376	3·76
22. 300 ml. medium+1 gm. C as Glucose +Chlorella+Tolypothrix + Azotobacter.	1·2102	1·2170	0·00383	3·83
23. 300 ml. medium+1 gm. C as Glucose +Chlorella + Tolypothrix+Rhizobium.	1·2102	1·2191	0·00385	3·85
24. 300 ml. medium+1 gm. C as Glucose +Chlorella+Tolypothrix + Azotobacter+Rhizobium.	1·2102	1·2193	0·00385	3·85
25. 300 ml. medium+1 gm. C as Glucose +Anabaena+Tolypothrix.	1·2102	1·2215	0·00387	3·87
26. 300 ml. medium+1 gm. C as Glucose +Anabaena+Tolypothrix + Azotobacter.	1·2102	1·2221	0·00388	3·88
27. 300 ml. medium+1 gm. C as Glucose +Anabaena+Tolypothrix + Rhizobium.	1·2102	1·2200	0·00389	3·89
28. 300 ml. medium+1 gm. C as Glucose +Anabaena+Tolypothrix + Azotobaxter+Rhizobium.	1·2102	1·2195	0·00391	3·91
29. 300 ml. medium+1 gm. C as Glucose + Chlorella + Anabaena + Tolypothrix.	1·2102	1·2218	0·00382	3·82
30. 300 ml. medium+1 gm. C as Glucose + Chlorella + Anabaena + Tolypothrix+Azotobacter.	1·2102	1·2201	0·00389	3·89
31. 300 ml. medium+1 gm. C as Glucose + Chlorella + Anabaena + Tolypothrix +Rhizobium.	1·2102	1·2202	0·00403	4·03
32. 300 ml. medium+1 gm. C as Glucose + Chlorella + Anabaena + Tolypothrix+Azotobacter+Rhizobium.	1·2102	1·2201	0·00403	4·03

The results recorded in the foregoing tables indicate that the association of Azotobacter and Rhizobium is not so much pronounced as compared to that of

bacteria and algae, as far as saving of carbon is concerned. This is probably due to the fact that the algae photosynthesize CO_2 into carbohydrates, which are made available to the bacteria. Lind and Wilson (1942) had also observed in their experiments that there is not pronounced effect in association of Azotobacter and Rhizobium.

Tolypothrix was found to be a more efficient fixer of nitrogen than Azotobacter or Chlorella. Similar results have also been observed in my experiment. The association of chlorella with bacteria does not show any marked influence on nitrogen fixation. The results do not support the viewpoint that chlorella and Azotobacter can grow in symbiosis wherein the alga supplies the carbohydrate and the bacteria fixes nitrogen as put forward by Russell (1961). However, there is slightly stimulating influence of chlorella on the growth and concomitant nitrogen fixation by Rhizobium. The results point out that chlorella may serve as host to Rhizobium and a symbiosis, unlike Azotobacter, is possible.

The association of Anabacna + Azotobacter, Anabaena+ Rhizobium and Anabaena+Azotobacter+Rhizobium are found to be similar in stimulating the fixation of nitrogen. There is saving of carbon and fixation of nitrogen are due to the capacity of Anabaena to utilize both CO_2 and nitrogen from the atmosphere.

Tolypothrix in the same way as in case of Anabaena, brought about greater nitrogen fixation. The association of Tolypothrix+Rhizobium is more pronounced than with Azotobacter in the beginning, the difference narrowing down in the end, *i.e.* after 170 days of exposure.

To sum up, it may be concluded that Tolypothrix either alone or in combination with Rhizobium or Anabaena, brought about a higher rate of nitrogen fixation, Azotobacter could not show a positive influence of its association with algae. Rhizobium, however, exhibited some potentials of positive influence in association with algae.

Summary

Effect of bacteria viz., Azotobacter, Rhizobium algae viz., Chlorella vulgaris, Anabaena neviculoides, Tolypothrix tenuis separately as well as in their assocaition were investigated in a composite medium containing the nutrients needed for Azotobacter, Rhizobium and Algae in presence of 1 gm. Carbon as glucose and light.

The association of Azotobacter and Rhizobium is not so much pronounced as compared to that of bacteria and algae, as far as saving of Carbon is concerned. This is due to fact that the algae photosynthesize CO_2 into Carbohydrate which are made available to the bacteria. Tolypothrix either alone or in combination with Azotobacter or Rhizobium brought about greater nitrogen fixation and more saving Carbon, presumably due to its higher efficiency of nitrogen fixation. Azotobacter could not show a positive influence of its association with algae as compared to Rhizobium with algae.

References

Allen, M. B. Photosynthetic Nitrogen Fixation by Blue Green Algae, 1955.

Lind, C. J. and Wilson, P. W. Nitrogen fixation. *Soil Ser.*, **54**(2) 105-11, 1942.

Russell, E. J. Soil Conditions and Plant Growth, 1961.

Waksman, S. A. Soil and Microbe, *John Wiley and Sons, Newyork*, 1931.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968

Some simple and interesting consequences of Landau's result

By

D. RAMESWAR RAO

Research Scholar, Department of Mathematics, Osmania University, Hyderabad-7

E. Landau obtained in [1] that $p = 1093$ is a solution of $2^{p-1} - 1 \equiv 0 \ (p^2)$. R. F. Whitehead improved Landau's proof of the same [2].

The object of this note is to show that $p = 1093$ satisfies all the following nine congruences simultaneously.

$$2^{p-1} - 1 \equiv 0 \ (p^2) \qquad (i)$$

$$2^{\frac{p-1}{2}} + 1 \equiv 0 \ (p^2) \qquad (ii)$$

$$2^k - 2^{k-l} + 2^{k-2l} - \ldots\ldots + 1 \equiv 0 \ (p^2) \text{ where } k = \frac{p - 2\overline{l+1}}{2},$$

$$l = 2 + 4x_n \ (n = 0, 1, 2, 3, 4, 9) \text{ or } 78 \qquad (iii)$$

x_n denoting the sum of first n natural numbers

By Euler's criterion $2^{\frac{1093-1}{2}} \equiv \left(\frac{2}{1093}\right) \ (1093)$

Since Euler proved that 2 is a quadratic non-residue of primes of the form $8n \pm 3$ [3], we get

$$2^{\frac{1093-1}{2}} + 1 \equiv 0 \ (1093) \qquad (1)$$

From Landau's result and (1), we get

$$2^{\frac{1093-1}{2}} + 1 \equiv 0 \ (1093^2) \qquad (2)$$

i.e., $(4 + 1)\ (4^{272} - 4^{271} + 4^{270} - \ldots\ldots + 1) \equiv 0 \ (1093^2)$

Since $(1093^2, 5) = 1$, we get

$$2^k - 2^{k-2} + 2^{k-4} - \ldots\ldots + 1 \equiv 0 \ (1093^2) \text{ where } k = \frac{1093 - \overline{2 \times 2 + 1}}{2} \qquad (3)$$

Writing (2) as $(2^6)^{91} + 1 \equiv 0 \ (1093^2)$, we have

$$(2^6 + 1)\ [\ (2^6)^{90} - (2^6)^{89} + (2^6)^{88} - \ldots\ldots + 1] \equiv 0 \ (1093^2)$$

But $(1093^2, 2^6 + 1) = 1$

$$\therefore 2^k - 2^{k-6} + 2^{k-12} - \ldots\ldots + 1 \equiv 0 \ (1093^2) \text{ where } k = \frac{1093 - 2\overline{\times 6 + 1}}{2} \qquad (4)$$

Writing (2) as $(2^{14})^{39} + 1 \equiv 0 \ (1093^2)$ we have

$$(2^{14} + 1)\ [\ (2^{14})^{38} - (2^{14})^{37} + (2^{14})^{36} - \ldots\ldots + 1] \equiv 0 \ (1093^2)$$

But $(1093^2, 2^{14}+1) = (1093^2, 5 \times 3277) = 1$

$$2^k - 2^{k-14} + 2^{k-28} - \ldots + 1 \equiv 0 \ (1093^2) \quad \text{where } k = \frac{1093 - \overline{2 \times 14+1}}{2} \tag{5}$$

Writing (2) as $(2^{26})^{21} + 1 \equiv 0 \ (1093^2)$

$$(2^{26}+1)\left[(2^{26})^{20} - (2^{26})^{19} + (2^{26})^{18} - \ldots + 1\right] \equiv 0 \ (1093^2)$$

But $2^{26}+1 = 4^{13}+1 = 5\left[4^{11}(4-1) + 4^9(4-1) + \ldots + 4(4-1) + 1\right]$

$$= 5\left[3 \times 4\,(4^{10} + 4^8 + \ldots + 4^2 + 4^0) + 1\right]$$

$$= 5 \times 1342\ 1773$$

$$\therefore (1093^2, 2^{26}+1) = 1$$

$$\therefore (2^{26})^{20} - (2^{26})^{19} + (2^{26})^{18} - \ldots + 1 \equiv 0 \ (1093^2)$$

$$\therefore 2^k - 2^{k-26} + 2^{k-52} - 2^{k-78} + \ldots + 1 \equiv 0 \ (1093^2) \text{ where } k = \frac{1093 - \overline{2 \times 26+1}}{2} \tag{6}$$

Writing (2) as $(2^{42})^{13} + 1 \equiv 0 \ (1093^2)$, we have

$$(2^{42}+1)\left[(2^{42})^{12} - (2^{42})^{11} + (2^{42})^{10} - \ldots + 1\right] \equiv 0 \ (1093^2)$$

But $2^{42}+1 = 4^{21}+1 = 5\,(4^{20} - 4^{19} + 4^{18} - \ldots + 1)$

$$= 5\left\{3\,(4^{19} + 4^{17} + \ldots + 4) + 1\right\}$$

$$= 5\left\{12\,(4^{18} + 4^{16} + \ldots + 4^0) + 1\right\}$$

$$= 5 \times 8796302221$$

$$\therefore (1093^2, 2^{42}+1) = 1$$

$$\therefore 2^k - 2^{k-42} + 2^{k-84} - \ldots + 1 \equiv 0 \ (1093^2) \text{ where } k = \frac{1093 - \overline{2 \times 42+1}}{2} \tag{7}$$

Similarly by writing (2) as $(2^{78})^7 + 1 \equiv 0 \ (1093^2)$ and $(2^{182})^3 + 1 \equiv 0 \ (1093^2)$

we get $2^k - 2^{k-78} + 2^{k-156} - \ldots + 1 \equiv 0 \ (1093^2)$ where $k = \frac{1093 - \overline{2 \times 78+1}}{2}$ (8)

and $2^k - 2^{k-182} + 2^{k-374} - \ldots + 1 \equiv 0 \ (1093^2)$ where $k = \frac{1093 - \overline{2 \times 182+1}}{2}$ (9)

Also, by writing $2 = 2 + 4(0)$, $6 = 2 + 4(1)$, $14 = 2 + 4\,(1+2)$,
$26 = 2 + 4(1+2+3)$, $42 = 2 + 4(1+2+3+4)$, $182 = 2+4\,(1+2+\ldots+9)$ (10)

we obtain (*iii*) from (3), (4), (5), (6), (7), (8), (9) and (10)

References

[1] E. Landau, Vorlesungen, *iii*, 275.

[2] G. H. Hardy and E. M. Wright, An Introduction to the Theory of Numbers, Fourth Edition, Chapter VI, 73.

[3] G. H. Hardy and E. M. Wright, An Introduction to the Theory of Numbers, Fourth Edition, Chapter VI, 75.

Proc. Nat. Acad. Sci., India, (38A) I & II, 1968

Physico-Chemical Properties of Milk Part IV, Adsorption of the Coagulation ions by Milk

By

SUDHISH CHANDRA & A. C. CHATTERJI

Chemistry Department, Lucknow University, Lucknow

[Received on 1st October, 1966]

Abstract

Both positive as well as negative ionic antagonisms were observed when milk was coagulated by different mixtures of electrolytes. An attempt was made to find out whether the coagulating ions play a role in producing ionic antagonism, by studying their adsorption and the effect of the second electrolyte on it. Cutting down in the adsorption of coagulating ions has been observed in the case of mixtures that show positive ionic antagonism and an increase is observed in the case of mixtures showing negative.

Introduction

The phenomenon of both positive as well as negative ionic antagonism has been observed by us (1) while coagulating milk with mixtures of electrolytes. The results reveal that the cations play the important role in producing ionic antagonism in the case of negatively charged milk sol. The positive ionic antagonism may be due to the cutting down in the adsorption of cations in the presence of the second electrolyte and negative due to an increase in it. It was thought, therefore, interesting to study the adsorption of the different coagulating ions and the effect of the second electrolyte on the adsorption of the cations of the first electrolyte so as to confirm the view put forward for the phenomenon of ionic antagonism.

Experimental

Two sets of bottles were taken and cleaned thoroughly with alkali, then with chromic acid and finally washed several times with distilled water and dried. In each of the one set of bottles, 25 ml of the milk sample were taken. In the other set a quantity of electrolyte sufficient to produce coagulation was taken in each bottle. To these bottles in turn were then added increasing amounts of the other electrolyte in the presence of which the effect on adsorption of the first electrolyte was to be studied. The total volume was made up in each case to 25 ml with distilled water. These two sets of bottles were then placed in an air thermostat. After some time, they were mixed together and allowed to stand for an hour inside the thermostat, after which the precipitates were filtered off and in the filterates the amount of the coagulating ions left were estimated. From these data were calculated the percentage amounts of the coagulating ions adsorbed.

Estimations of Aluminium : Aluminium was estimated by adding to the solution an excess of EDTA solution which forms a complex with it readily, then the excess of EDTA was titrated against Manganese sulphate using Eriochrome Black T as indicator (2).

Estimation of Iron : For the estimation of Iron a slight excess of ammonia was added to solution and the precipitate was filtered. The precipitate was dissolved in dilute HCl and to this solution KCNS was added when a red colour was produced. The strength was obtained by the help of a Klett-Summerson's Colorimeter (3).

Estimation of Zinc : Zinc solution was titrated against $K_4Fe(CN)_6$ using Diphenyl-amine as indicator (4).

Estimation of Copper : From the solution free mineral acids were removed by adding Na_2CO_3 until a faint permanent precipitate remained and this was then redissolved by adding a few drops of CH_3COOH. To this solution, KI was added and the liberated I_2 was titrated against sodium thiosulphate solution (5).

Estimation of Hydrogen ions : Hydrogen ions were estimated by pH measurements with a Pye pH meter.

Results and Discussion

TABLE I

Adsorption of Al^{+++} in presence of $Cu(NO_3)_2$

Sol. – 50 % milk Temp. – 25°C

Conc. of $Al(NO_3)_3$ m.M./l	Conc. of $Cu(NO_3)_2$ m.M./l	Conc. of Al^{+++} in filtrate m.M./l	Al^{+++} adsorbed m.M./l	Percentage adsorption
5·0	–	0·26	4·74	94·80
5·0	1·0	0·32	4·68	93·60
5·0	1·5	0·37	4·63	92·60
5·0	2·0	0·43	4·57	91·40
5·0	2·5	0·48	4·52	90·40

TABLE II

Adsorption of Al^{+++} in presence of HNO_3

Sol. – 50 % milk Temp. – 25°C

Conc. of $Al(NO_3)_3$ m.M./l	Conc. of HNO_3 m.M./l	Conc. of Al^{+++} in filtrate m.M./l	Al^{+++} adsorbed m.M/l	Percentage adsorption
5·0	–	0.26	4·74	94·80
5·0	2·0	0·33	4·67	93·40
5·0	4·0	0·37	4·63	92·60
5·0	6·0	0·42	4·58	91·60
5·0	8·0	0·49	4·51	90·20

TABLE III

Adsorption of Fe^{+++} in presence of $Zn(NO_3)_2$

Sol. – 50% milk Temp. – 25°C

Conc. of $Fe(NO_3)_3$	Conc. of $Zn(NO_3)_2$	Conc. of Fe^{+++} in filtrate m.M./l	Fe^{+++} adsorbed m.M./l	Percentage adsorption
5·0	–	0·28	4·72	94·40
5·0	1·0	0·33	4·67	93·40
5·0	1·5	0·36	4·64	92·80
5·0	2·5	0·40	4·60	92·00
5·0	2·5	0·44	4·56	91·20

TABLE IV

Adsorption of Zn^{++} in presence of $Al(NO_3)_3$

Sol. – 50% milk Temp. – 25°C

Conc. of $Zn(NO_3)_2$ m.M./l	Conc. of $Al(NO_3)_3$ m.M./l	Conc. of Zn^{++} in filtrate m.M./l	Zn^{++} adsorbed m.M./l	Percentage adsorption
6·0	–	0·64	5·36	89·33
6·0	1·0	0·54	5·46	91·00
6·0	1·5	0·50	5·50	91·66
6·0	2·0	0·46	5·54	92·33
6·0	2·5	0·40	5·60	93·33

TABLE V

Adsorption of Zn^{++} in presence of $Fe(NO_3)_3$

Sol. – 50% milk Temp. – 25°C

Conc. of $Zn(NO_3)_2$ m.M./l	Conc. of $Fe(NO_3)_3$ m.M./l	Conc. of Zn^{++} in filtrate m.M./l	Zn^{++} adsorbed m.M./l	Percentage adsorption
6·0	–	0·64	5·36	89·33
6·0	1·0	0·73	5·27	87·83
6·0	1·5	0·76	5·24	87·33
6·0	2·0	0·80	5·20	86·66
6·0	2·5	0·86	5·14	85·66

TABLE VI

Adsorption of Zn^{++} in presence of HNO_3

Sol. – 50% milk Temp. – 25°C

Conc. of $Zn(NO_3)_2$ m.M./l	Conc. of HNO_3 m.M./l	Conc. of Zn^{++} in filtrate m.M./l	Zn^{++} adsorbed m.M./l	Percentage adsorption
6·0	–	0·64	5·36	89·33
6·0	2·0	0·53	5·47	91·16
6·0	4·0	0·49	5·51	91·83
6·0	6·0	0·45	5·56	92·66
6·0	8·0	0·36	5·64	94·00

TABLE VII

Adsorption of Cu^{++} in presence of $Al(NO_3)_3$

Sol. – 50% milk Temp. – 25°C

Conc. of $Cu(NO_3)_2$ m.M./l	Conc. of $Al(NO_3)_3$ m.M./l	Conc. of Cu^{++} in filtrate m.M./l	Cu^{++} adsorbed m.M./l	Percentage adsorption
5·5	–	0·50	5·00	90·91
5·5	1·0	0·59	4·91	89·27
5·5	1·5	0·66	4·84	88·00
5·5	2·0	0·74	4·76	86·54
5·5	2·5	0·86	4·64	84·36

TABLE VIII

Adsorption of Cu^{++} in presence of HNO_3

Sol. – 50% milk Temp. – 25°C

Conc. of $Cu(NO_3)_2$ m.M./l	Conc. of HNO_3 m.M./l	Conc. of Cu^{++} in filtrate m.M./l	Cu^{++} adsorbed m.M./l	Percentage adsorption
5·5	–	0·50	5·00	90·91
5·5	2·0	0·60	4·90	89·09
5·5	4·0	0·68	4·82	87·64
5·5	6·0	0·75	4·75	86·36
5·5	8·0	0·86	4·64	84·36

TABLE IX

Adsorption of Cu^{++} in presence of H_2SO_4

Sol. – 50% milk Temp. – 25°C

Conc. of $Cu(NO_3)_2$ m.M./l	Conc. of H_2SO_4 m.M./l	Conc. of Cu^{++} in filtrate m.M./l	Cu^{++} adsorbed m.M./l	Percentage adsorption
5·5	–	0·50	5 00	90·91
5·5	1·0	0·59	4·91	89·27
5·5	2·0	0·64	4·86	88·36
5·5	3·0	0·75	4·75	86·36
5·5	4·0	0·84	4·66	84·73

TABLE X

Adsorption of H^+ in presence of $Zn(NO_3)_2$

Sol. – 50% milk Temp. – 25°C

Conc. of HNO_3 m.M./l	Conc. of $Zn(NO_3)_2$ m.M./l	Conc. of H^+ in filtrate m.M./l	H^+ adsorbed m.M./l	Percentage adsorption
20·0	–	0·004	19·996	99·98
20·0	1·0	0·012	19·988	99·94
20·0	1·5	0·020	19·980	99·90
20·0	2·0	0·027	19·973	99·87
20·0	2·5	0·031	19·969	99·85

TABLE XI

Adsorption of H^+ in presence of $Cu(NO_3)_2$

Sol. – 50% milk Temp. – 25°C

Conc. of HNO_3 m.M./l	Conc. of $Cu(NO_3)_2$ m.M./l	Conc. of H^+ in filtrate m.M./l	H^+ adsorbed m.M./l	Percentage adsorption
20·0	–	0·004	19·996	99·98
20·0	1·0	0·010	19·990	99·95
20·0	1·5	0·018	19·982	99·91
20·0	2·0	0·025	19·974	99·87
20·0	2·5	0·032	19·968	99·84

It has been observed that the adsorption of Al^{+++} ions decreases as we go on increasing the concentration of Cu^{++} ions or H^+ ions in the electrolytic mixture. Similarly the adsorption of Fe^{+++} ions in presence of Zn^{++} ions of Zn^{++} ions in the presence of Fe^{+++} ions, of Cu^{++} ions in presence of Al^{+++} ions and H^+ ions also decreases, whereas the adsorption of Zn^{++} ions in presence of Al^{+++} and H^+ ions increases. A very slight decrease (0·13 - 0 14%) in the adsorption of H^+ ions is observed in the presence of Cu^{++} and Zn^{++} ions, which may, therefore, be considered to remain practically unchanged.

It was observed by us (loc. cit.) that when milk is coagulated by a mixture of electrolytes such as $Cu(NO_3)_2 + Al(NO_3)_3$, $Cu(NO_3)_2 + HNO_3$, $Cu(NO_3)_2 + H_2SO_4$ and $Zn(NO_3)_2 + Fe(NO_3)_3$, positive ionic antagonism is observed which may be due to the mutual cutting down in adsorption of coagulating ions. The present studies on adsorption also show that cutting down in adsorption of coagulating ions takes place in the case of these mixtures of electrolytes. In the case of negative ionic antagonism which is observed with the mixtures like $Zn(NO_3)_2 + Al(NO_3)_3$ and $Zn(NO_3)_2 + HNO_3$ the adsorption studies show an incrcase in the absorption of Zn^{++} ions in the presence of Al^{+++} and H^+ ions. These results confirm the author's view that probably the coagulating ions play an important role in ionic antagonism observed with the mixture of electrolytes. In the presence of the second electrolyte the cutting down or increase in adsorption of the coagulating ion of the electrolytes takes place, and so the values obtained with the mixtures of electrolytes are not additive but either lower than additive, or higher, according as an increase or decrease in adsorption takes place respectively.

Also it has been observed that H^+ ions are adsorbed the most and since the coagulation depends upon the adsorption of the coagulating ions, the deviation (6) from Schulze - Hardy rule which has also been observed by Puri and Prakash (7) can be explained. In the case of coagulation with acids, the H^+ ions are adsorbed to the extent of 99·98% whereas Zn^{++} and Cu^{++} ions are adsorbed to the extent of 89·33 and 90·91% respectively. Since the adsorption of univalent H^+ ion is higher than that of bivalent Cu^{++} and Zn^{++} ions lesser quantities of the acids are required to coagulate milk than that of Cu and Zn salts, though according to Schulze-Hardy rule the reverse should have been the case.

Acknowledgements

One of the author (S. C.) is thankful to Prof. S. N. Shukla, ex-Head of the Chemistry Department, Lucknow University and Dr. R. S. Srivastava, Public Analyst to U. P. Government for their interest. He is also thankful to the Scientific Research Committee, Allahabad for the grant that enabled this work to be carried out.

References

1. S. Chandra and A. C. Chatterji. *Proc. Natl. Acad. Sci. (India)* **35A** : 137, 1965.
2. J. Kinnunen and B. Merikanto. Chemist Analyst, **44** : 75, 1955.
3. A. I. Vogel. A test book of Quantitative Inorganic Analysis, III edition, 785, 1961.
4. A. I. Vogel. A text book of Quantitative Inorganic Analysis, III edition, 401, 1961.
5. A. I. Vogel. A text book of Quantitative Inorganic Analysis, III edition, 358, 1961.
6. S. Chandra. *Proc. Natl. Acad. Sci. (India)* **33A** : 17, 1963.
7. B. R. Puri and S. Prakash. *J. Indian Chem. Soc.*, **39** : 605, 1962.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968.

Effect of rotation on Rayleigh-Taylor Instability of Compressible Fluids

By

P. K. BHATIA

Department of Mathematics, University of Jodhpur, Jodhpur

[Received on 14th May, 1967]

The stability problem of an accelerating plane interface separating compressible fluids has been studied earlier by Mitchner and Landshoff. In the present work the same problem has been extended to include the effect of uniform rotation about an axis. In the limit of small wave length disturbances, the stability criterion has been obtained. It is found that the criterion is not affected by the presence of rotation.

1. Introduction

Taylor (1950) studied the problem of the stability of a plane interface separating two incompressible fluids in a constant gravitational field. Recently Mitchner and Landshoff (1964) have considered the more general problem of the stability of an accelerating (non constant) contact surface separating compressible fluids. In the limit of small wave length disturbances, they obtained a generalized form of Taylor's value for the growth rate. They also showed that for the particular case of constant acceleration and static isothermal equilibrium, the stability criterion remains the same as for corresponding case of two incompressible fluids, but the growth rate is reduced for longer wavelengths.

The present work is concerned with the stability problem of accelerating (non-constant) contact surface separating two compressible fluids when the configuration is in uniform rotation, with angular velocity Ω, about an axis. The study thus includes the effect of uniform rotation on the problem considered by Mitchner and Landshoff. The stability criterion has been obtained in the limit of small wavelength disturbances.

2. Formulation of the Problem

Let us consider a situation in which the equation $X = \xi(t)$, a fn. of time, specifies the location of a plane interface in an inertial frame (X, Y, Z). The system is assumed to rotate about x-axis with a uniform angular velocity Ω. We require to investigate the stability of the plane interface.

In a frame of reference (x, y, z) attached to the unperturbed interface, the motion of the fluids on both the sides of the interface is governed by the equation of continuity

$$\frac{d\rho_t}{dt} + \rho_t \nabla . \vec{v_t} = 0 \tag{1}$$

and the equations of motion

$$\rho_t \frac{\vec{dv_t}}{dt} + \nabla P + \rho_t \ddot{\xi}(t) \hat{x} + \tfrac{1}{2} \rho_t \frac{\partial}{\partial x_i} (|\vec{\Omega} \times \vec{r}|^2) - 2 \rho_t \varepsilon_{ijk} v_{tj} \Omega_k = 0, \tag{2}$$

In equations (1) and (2) ρ_t is the density, $\vec{v_t}$ is the velocity, P is the pressure and $\hat{x}$ is a unit vector in the direction of x- axis. Further we assume that the motion is adiabatic so that in this case the energy equation is given by

$$\rho_t \frac{dP}{dt} = \gamma P \frac{d\rho_t}{dt}, \tag{3}$$

where γ is the ratio of specific heats and is assumed to be constant (with value $1 < \gamma \leqslant 5/3$).

If the fluids initially occupy the regions $x > 0$ and $x < 0$ and are distinguished by the superscripts + and – respectively then the function defining the equation of the interface surface $f(x, y, z, t) = 0$ must satisfy the equation

$$\frac{\partial f}{\partial t} + \vec{V_s}^{\pm} \nabla f = 0, \tag{4}$$

where the subscript s denotes a value on the perturbed surface. The fluids must, therefore, satisfy the matching condition

$$\vec{V_s}^{-} \hat{N} = \vec{V_s}^{+} \hat{N} \tag{5}$$

where $\hat{N} = \frac{\nabla f}{|\nabla f|}$ is the unit normal to the interface. If we integrate the momentum equation (2) across the interface we obtain a second matching condition

$$P_s^{-} = P_s^{+} \tag{6}$$

Assuming that the unperturbed motion $\rho_0 = \rho_0 (x, t)$, $\vec{V_0} = [u_0 (x, t), 0, 0]$ $p_0 = p_0 (x, t)$ satisfies equations (1) – (3), (5) and (6) and by writing the perturbations in the various physical quantities as

$$\left.\begin{aligned} \rho_t &= \rho_0 + \rho_1 (x, t) \exp (i \vec{k}. \vec{r}), \\ \vec{v_t} &= \vec{V_0} + \vec{v_1} (x, t) \exp (i \vec{k}. \vec{r}), \\ P &= p_0 + p_1 (x, t) \exp (i \vec{k}. \vec{r}), \\ \hat{N} &= \hat{x} + n_1 (x, t) \exp (i \vec{k}. \vec{r}), \end{aligned}\right\} \tag{7}$$

where $\vec{r} = (x, y, z)$, $\vec{k} = (0, k_y, k_z)$, $\vec{v_1} = (u_1, v_1, w_1)$,
we can obtain the linearized perturbation equations.

It may be mentioned that in the problems of stability of plane interface separating two fluids, arranged in horizontal strata, the density and pressure are taken to vary only with the vertical coordinate *i.e.* p and ρ do not vary with coordinates perpendicular to the vertical coordinate. In the present problem the fluids occupy the regions $x > 0$ and $x < 0$. and the configuration is in uniform rotation about the x-axis. Consequently the density, in the rotating system does not vary with coordinates perpendicular to the axis of rotation.

If we substitute equations (7) in equations (1) – (3) and linearize, we obtain

$$\left(\frac{d}{dt}+\frac{\partial u_0}{\partial x}\right)\rho_1+\frac{\partial}{\partial x}(\rho_0 u_1)+i\rho_0\vec{k}.\vec{v}_1=0, \tag{8}$$

$$-\frac{1}{\rho_0}\frac{\partial p_0}{\partial x}\rho_1+\rho_0\left(\frac{du_1}{dt}+\frac{\partial u_0}{\partial x}u_1\right)+\frac{\partial p_1}{\partial x}=0, \tag{9a}$$

$$-2\rho_0\Omega w_1+\rho_0\frac{dv_1}{dt}+ik_y p_1=0, \tag{9b}$$

$$2\rho_0\Omega v_1+\rho_0\frac{dw_1}{dt}+ik_z p_1=0, \tag{9c}$$

$$a^2\left(\frac{d}{dt}-\frac{1}{\rho_0}\frac{d\rho_0}{dt}\right)\rho_1+\left(a^2\frac{\partial\rho_0}{\partial x}-\frac{\partial p_0}{\partial x}\right)u_1-\left(\frac{d}{dt}-\frac{\gamma}{\rho_0}\frac{d\rho_0}{dt}\right)p_1=0, \tag{10}$$

where a^2 is the sound speed given by

$$a^2=\frac{\gamma p_0}{\rho_0} \tag{11}$$

and $\frac{d}{dt}$ is the mobile operator

$$\frac{d}{dt}=\frac{\partial}{\partial t}+\vec{V}_0\cdot\nabla=\frac{\partial}{\partial t}+u_0\frac{\partial}{\partial x} \tag{12}$$

In order to write the linearized matching conditions, let us write the equation of the interface in the form

$$x=x_1(t)\exp(i\vec{k}.\vec{r}) \tag{13}$$

and then, from equations (5) – (7), we obtain

$$x_1\left(\frac{\partial u_0^-}{\partial x}\right)_{x=0}+u_1^-(0,t)=x_1\left(\frac{\partial u_0^+}{\partial x}\right)_{x=0}+u_1^+(0,t), \tag{14}$$

$$x_1\left(\frac{\partial p_0^-}{\partial x}\right)_{x=0}+p_1(0,t)=x_1\left(\frac{\partial p_0^+}{\partial x}\right)_{x=0}+p_1^+(0,t) \tag{15}$$

wherein we have used the fact that $u_0^{\pm}(o,t)=0$, which follows from the consideration that $x=0$ is a contact surface. Also from equation (4), we may get

$$x_1\left(\frac{\partial u_0^{\pm}}{\partial x}\right)_{x=0}+u_1^{\pm}(0,t)=\frac{\partial x_1}{\partial t}. \tag{16}$$

The interface is unstable if there exist any initial perturbations which develop in time in accordance with the flow and matching equations (together with suitable boundary conditions at $x=\pm\infty$) and which do not remain bounded as $t\to\infty$.

3. Quasi Steady State Assumptions

Let us suppose that in the accelerating frame, the time scales of the unperturbed and perturbed motions are of order T and τ respectively. Restricting the analysis to perturbations for which

$$\tau<<T \tag{17}$$

the coefficients in equations (8) - (10) may be regarded as functions of x only and we may seek perturbation solutions of the form

$$\left.\begin{aligned} x_1(t) &= x_s \exp(nt), \qquad |n| \sim 0\,(1/\tau) \\ p_1(x, t) &= p(x) \exp(nt), \\ \rho_1(x, t) &= \rho(x) \exp(nt), \end{aligned}\right\} \tag{18}$$

with similar expressions for $\vec{v_1}(x, t)$ *i.e.* for u_1, v_1, w_1.

From the mass conservation of unperturbed motion, $\frac{\partial u_0}{\partial x} \sim 0\left(\frac{1}{\tau}\right)$. Using the assumption (17) and the expressions (18) we may eliminate v and w between equations (8) and (9*b*) - (9*c*).

Equation (8) can be written as

$$\left(n + u_0 \frac{d}{dx}\right)\rho + \frac{d}{dx}(\rho_0 u) + i\rho_0 (k_y v + k_z w) = 0, \tag{19}$$

which, with the help of the following relation between v and w [*See* Appendix]

$$\rho_0(ik_y v + ik_z w) = \frac{k^2\left(n + u_0 \frac{d}{dx}\right)}{\left[\left(n + u_0 \frac{d}{dx}\right)^2 + 4\Omega^2\right]} p, \tag{20}$$

reduces to

$$\left(n + u_0 \frac{d}{dx}\right)^3 \rho + \left\{\left(n + u_0 \frac{d}{dx}\right)^2 + 4\Omega^2\right\} \frac{d}{dx}(\rho_0 u) + \left(n + u_0 \frac{d}{dx}\right)(k^2 p + 4\Omega^2 \rho) = 0. \tag{21}$$

With the help of (17) and (18), equations (9*a*) and (10), (14) - (16) can be rewritten in the form

$$\frac{-p_0'}{\rho_0}\rho + \left(n + u_0 \frac{d}{dx}\right)(u\rho_0) + \frac{dp}{dx} = 0, \tag{22}$$

$$a^2\left(n + u_0 \frac{d}{dx}\right)\rho + \frac{1}{\rho_0}\left(a^2 \frac{d\rho_0}{dx} - \frac{dp_0}{dx}\right)(u\rho_0) - \left(n + u_0 \frac{d}{dx}\right) p = 0, \tag{23}$$

$$u^{\pm}(o) = nx_s \tag{24}$$

$$p^+(o) - p^-(o) = \left[\left(\frac{dp_0^-}{dx}\right)_{x=o} - \left(\frac{dp_0^+}{dx}\right)_{x=o}\right] x_s \tag{25}$$

The motion of each fluid in terms of the growth rate n is determined by equations (21) - (23). The arbitrary constant associated with the homogeneous character of these equations is fixed by equation (24) whereas equation (25), then, provides an equation for the determination of growth rate n.

The analysis is greatly simplified if we make the following assumption. If l is a characteristic length scale of the perturbed motion, then $u_0\left(\frac{d}{dx}\right) \sim 0\left(\frac{u_0}{l}\right)$.

Restricting the analysis to perturbations satisfying the condition (as in Mitchner and Landshoff).

$$(u_0 \tau/l)\,(\tau/T) << 1, \tag{26}$$

we obtain, from equations (22) and (23)

$$\rho_0 u(x) = \frac{1}{n\alpha}\left(\frac{p_0'}{\gamma p_0} - \frac{d}{dx}\right) p, \tag{27}$$

$$n^2\rho(x) = \frac{1}{\alpha}\left[\left(\frac{n}{a}\right)^2 + \left(\frac{\rho_0'}{\rho_0} - \frac{p_0'}{\gamma\rho_0}\right)\frac{d}{dx}\right] p, \tag{28}$$

where

$$\alpha(x) = 1 + \left(\frac{a}{n}\right)^2 \frac{p_0'}{\gamma p_0}\left(\frac{\rho_0'}{\rho_0} - \frac{p_0'}{\gamma p_0}\right), \tag{29}$$

$$p_0' = \frac{dp_0}{dx}, \quad \rho_0' = \frac{d\rho_0}{dx}.$$

Within the preceding restriction, substituting (27) and (28) in equation (21), we obtain a single equation for $p(x)$.

$$\frac{d^2p}{dx^2} - (\log \rho_0 \alpha)' \frac{dp}{dx} - \left[\frac{k^2 n^2 a}{n^2 + 4\Omega^2} + \frac{n^2}{a^2} + \alpha\left(\frac{p_0'/\gamma p_0}{a}\right)'\right] p = 0, \tag{30}$$

where dash means differentiation with respect to x. The condition (26) may be viewed as an additional requirement of a quasisteady state in the accelerated frame, in the sense that u_0 must not be "too large".

4. Limit of Small Wavelength

Making all the assumptions of limit of small wave length disturbances as in Mitchner and Landshoff, equations (30) and (27), in the present case, reduce to

$$\frac{d^2p}{dx^2} - K^2 p = 0, \tag{31}$$

$$\rho_0 u(x) = -\frac{1}{n}\frac{dp}{dx} \tag{32}$$

where

$$K^2 = \frac{k^2}{1 + 4\Omega^2/n^2} \tag{33}$$

With the requirement that the perturbed motion should vanish at $x = \pm\infty$, it follows from equation (31) that $p^{\pm}(x) = p^{\pm}(o)\exp(\mp K x)$. Therefore, from equations (32) and (24), we then obtain

$$p^{\pm}(o) \equiv \pm n^2 \rho_{\pm} x_p/K \tag{34}$$

wherein we have written $\rho_{\pm} = \rho_0^{\pm}(o)$.

Substituting (34) into equation (25) yields the equation for the growth rate n

$$n^2\left(1 + \frac{4\Omega^2}{n^2}\right)^{\frac{1}{2}} = k\,\frac{\left(\frac{dp_0^-}{dx}\right)_{x=o} - \left(\frac{dp_0^+}{dx}\right)_{x=o}}{\rho_+ + \rho_-}, \tag{35}$$

or

$$n^2\left(1 + \frac{4\Omega^2}{n^2}\right)^{\frac{1}{2}} = n_0^2, \tag{36}$$

where n_0^2 is the value of n appropriate for the wave number k in the absence of rotation. The solution of equation (36) is

$$n^2 = -2\Omega^2 + \sqrt{4\Omega^4 + n_0^4}, \quad \text{if } n_0^2 > 0 \tag{37}$$

and

$$n^2 = -2\Omega^2 - \sqrt{4\Omega^4 + n_0^4}, \quad \text{if } n_0^2 < 0 \tag{38}$$

From equations (37) and (38) it follows that in the present case of small wavelength disturbances and compressible fluids, the rotation does not effect the instability or stability. We find that

It has been shown [Mitchner and Landshoff] that for the case under study, in the absence of rotation, the interface is unstable when the slope of the unperturbed pressure decreases in the direction of increasing pressure, and is stable otherwise as it is clear from value of n_0^2 given by equation (35).

We thus conclude that the stability criterion remains uneffected by the presence of rotation in the compressible fluids also.

Appendix

Substituting (18) for v_1, w_1 and p_1 in equations (9*b*) and (9*c*) and then multiplying (9*b*) by $-ik_y$ and (9*c*) by $-ik_z$ and adding, we get

$$2\rho_0\Omega\xi - \rho_0\left(n + u_0\frac{d}{dx}\right)(ik_y v + ik_z w) = -k^2 p, \tag{39}$$

where

$$\xi = ik_y w - ik_z v, \tag{40}$$

is the u-component of the vorticity.

Again, by multiplying (9*b*) by $-ik_z$ and (9*c*) by $+ik_y$ and adding, we get

$$\left(n + u_0\frac{d}{dx}\right)\xi + 2\Omega(ik_z w + ik_y v) = 0. \tag{41}$$

Therefore

$$\xi = -\frac{2\Omega(ik_y v + ik_z w)}{(n + u_0\, d/dx)} \tag{42}$$

Substituting the value of ξ in (39), we get

$$\rho_0(ik_y v + ik_z w) = \frac{k^2\left(n + u_0\frac{d}{dx}\right)}{\left[\left(n + u_0\frac{d}{dx}\right)^2 + 4\Omega^2\right]} p. \tag{43}$$

References

1. Mitchner, M. and Landshoff, K. M. *Phys. of Fluids*, 7 : No. 6, 862, 1964.
2. Taylor, G. I. *Proc. Roy. Soc. (London)*, **A201** : 192, 1950.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968

Amino acids content of Neem seed cake

By

N. P. SINHA[1] AND K. C. GULATI[2]

[Recevied on 24th October, 1966]

Oil seeds constitute an important economic crop of India and oil cakes are valuable and major bye-product of oil extraction industry. The cakes from edible oil seeds are utilised as cattle feed and those from non-edible oil seeds are exclusively used as manure. Neem seed cake is obtained by crushing the whole seed or Kernel and thereby, the lipids and cakes are separated.

Neem seed cake, as obtained from Wardha Ghani system contains certain amount of oils and appreciable quantity of bitter and odoriferous substances. The glycerides present in the cake have been first extracted with petroleum ether and the remaining bitter and odoriferous substances have subsequently been extracted with alcohol. The residual cake has been found to be practically tasteless and odourless and may safely be used as a feed for the cattle (Sinha 1960). The value of oil cakes as a feed largely depends on the amount of protein and nature and extent of different amino acids present. Hence, in the present work, attempt has been made to assay the processed neem seed cake for amino acid content.

Methods and Materials : A weighed (1·0 gm) amount of cake was taken and treated with petroleum ether and then with alcohol. It was then hydrolysed with 25 ml, 5·6 N HCl in an autoclave at a pressure of 115 lb/sq inch and 120°C temperature for about 8 hours.

After hydrolysis it was made free from hydrochloric acid by repeated evaporation on water bath while adding distilled water.

The descending technique of paper chromatography as described by Consden *et al.* (1944) was employed. The chromatogram was run for 16 hours at 28 ±2°C. The chromatogram was developed by spraying 0·2 per cent ninhydrin solution in butanol and their Rf values were calculated.

Column Chromatography : Resin column was used for amino acids analysis. The resin was first equilibrated with a suitable buffer solution and then a sample of amino acid mixture in the buffer was added to the column. For acid and neutral amino acids 150 cm. long column was used and for basic amino acids 30 cm. long column was employed. Method as given by Moore, Spackman and Stein (1958) was followed with ion exchange resin particles as given by Hammilton (1958).

For tryptophan, hydrolysis was done with 5N NaOH and determined by method of Sullivan and Hess (1944).

Results and discussion : The processed neem seed cake was analysed qualitatively for different amino acids by two dimensional method of paper chromatography. The amino acids identified on the paper with the help of stanndard,

1. Dr. N. P. Sinha, M.Sc., Ph.D., Professor of Agricultural Chemistry, Tirhut College of Agriculture, Dholi, Muzaffarpur, Bihar.

2. Dr. K. C. Gulati, M.Sc., Ph.D., Professor of Chemistry, Indian Agricultural Research Institute, New Delhi.

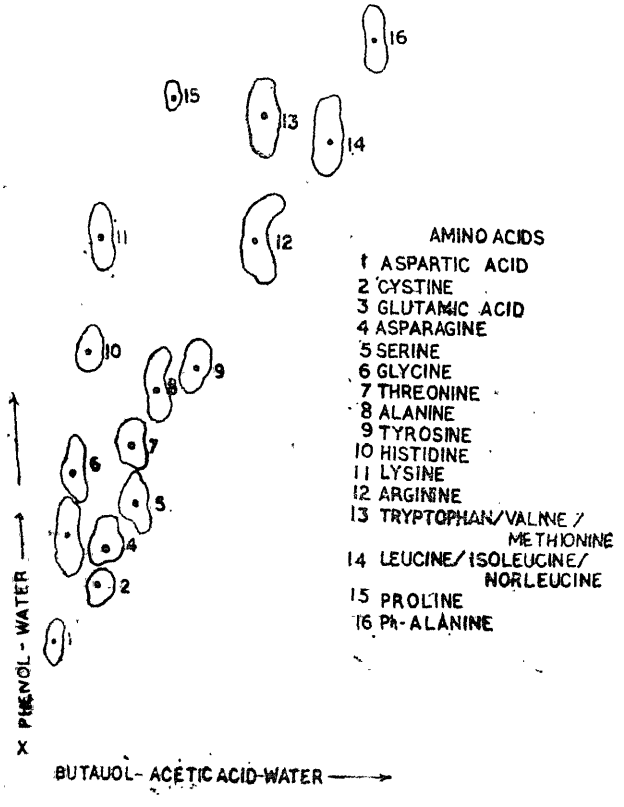
were aspartic acid, cystine, glutamic acid, asparagine ; serine ; glycine ; threonine ; alanine ; tyrosine ; histidine ; lysine ; hydroxyproline ; arginine ; tryptophan ; valine ; methionine ; leucine ; iso-leucine ; norleucine ; proline and phenylalanine.

The Rf values of tryptophan, valine and methionine were very close to each other and so it became difficult to identify them seperately. Similar was the case with leucine, isoleucine, and norleucine. These two groups of amino acids gave only one spot for each of the three amino acids. Thus, any one of them or mixture of all might be present.

Chromatogram showing actual relative positions of amino acids in the processed neem and cake has been shown in fig. 1.

FIG I

CHROMATOGRAM SHOWING ACTUAL RELATIVE POSITION OF AMINO ACIDS IN PROCESSESED NEEMSEED CAKE



The quantitativt analysis of amino acids in processed neem seed cake is shown in fig. 2. The quanəties of amino acids present in the processed neem seed cake are given in table 1.

From the table it appears that processed neem seed cake is rich in most of the essential amino acids except valine and tryptophan. The cake contains methionine (3·23%) and cysteic acid (0·56%) which are sulphur containing amino acids. The contents of glutamic acid are the highest of all amino acids present. Valine and tryptophan were found to be almost negligible, hence not suitable as a protein feed and food.

In the quantitative estimation, the total percentage of amino acids in terms of protein as accounted for was 45·34 per cent as against 46·87 per cent (total protein content of processed neem seed cake). On the basis of 16 gm nitrogen, (in 100 gm protein) which is usually employed for calculating amino acids in proteins, it comes to 96·58 per cent as against 100.

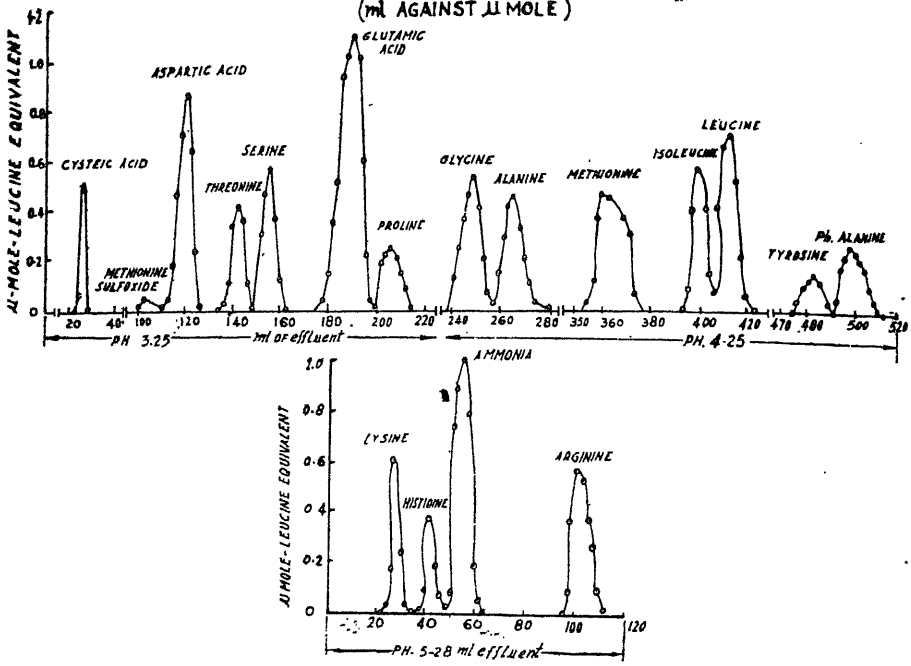
TABLE 1

Amino acids content of neem seed cake (processed) as obtained by column chromatography

Sl. No.	Amino Acids	Percent basis	On 16 gm N basis
1.	Cysteic acid	0·560	1·192
2.	Methionine sulphoxide	0·055	0·117
3.	Aspartic acid	5·020	10·692
4.	Threonine	1·802	3·838
5.	Serine	2·550	5·431
6.	Glutamic acid	10·125	21·566
7.	Proline	1·103	2·349
8.	Glycine	0·993	2·115
9.	Alanine	1·990	4·238
10.	Methionine	3·226	6·871
11.	Isoleucine	2·210	4·707
12.	Leucine	3·514	7·484
13.	Tyrosine	1·257	2·677
14.	Phenyl alanine	3·113	6·630
15.	Lysine	2·309	4·918
16.	Histidine	1·268	2·700
17.	Arginine	3·526	7·510
18.	Tryptophan	Traces	Traces
19.	Others	0·727	1·548
	Total	43·343	96·583

Fig. II

AMINO ACID AS OBTAINED IN COLUMN CHROMATOGRAPHY
(ml AGAINST μ MOLE)



Two of the amino acids, proline and hydroxy proline which are not alpha amino acids and do not contain NH_2 group, did not produce blue colour with ninhydrin solution and so were not read at 55 mμ wave length in colorimeter. Like all other amino acids they developed yellow color with ninhydrin which was read at 44 mμ wave length.

As mentioned above, neem seed cake is outstanding in the content of methionine and lysine, the two essential amino acids in which most of the vegetable proteins are lacking. However, the two amino acids--valine and tryptophan limit its protein value ; the former is found abundantly and the latter moderately in many of the vegetable proteins.

References

1. Consden, R., Gordon, A. H. and Martin, A. J. P. *Biochem, J.* **38** : 224-332, 1944.
2. Moore, S., Spackman, D. H. and Stein, W. H. *Annal. Chem.*, **30** (7) : 1185 1190, 1958.
3. Hamilton, Paul, B. *Annal, Chem.*, **30** : 914, 1958.
4. Sullivan, M. X. and Hess, W. C. *J. Biol. Chem.* **155** : 441-446, 1944.
5. Sinha, N. P. Thesis submitted for M.Sc. (Ag.) degree at Indian Agril. Res. Instt., New Delhi, 1960.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968

Two Theorems on H-Function of Fox

By

RATTAN SINGH

Deptt. of Mathematics, Govt. Science College, Rewa, M. P.

[Received on 18th October, 1966]

Abstract

Fox has defined a function, more general than Meijer's G-function in the form :

$$H(x) = \frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} \frac{\prod_{j=1}^{q}\Gamma(b_j + c_j.s)\ \prod_{j=1}^{p}\Gamma(a_j - e_j.s)}{\prod_{j=1}^{q}\Gamma(b_j + c_j - c_j.s)\ \prod_{j=1}^{p}\Gamma(a_j - e_j + e_j.s)}\ x^{-s}\,ds$$

where $c_j > 0, j = 1, 2, \ldots, q, \quad e_j > 0, j = 1, 2, \ldots, p, q \geqslant p + 1$ and all the poles of the integrand are simple.

In the present note, the author establishes two theorems, one is the generalization of Edelstein's Addition Theorem on G-function while the other deals with the evaluation of an integral involving product of two H-functions from which a good many results on G-function and other functions appearing in Applied Mathematics and Mathematical Physics may be deduced as particular cases.

1. Introduction : Fox (3, p. 408) has defined a function

$$H(x) = \frac{1}{2\pi i}\int_{\sigma-i\infty}^{\sigma+i\infty} \frac{\prod_{j=1}^{q}\Gamma(b_j + c_j.s)\ \prod_{j=1}^{p}\Gamma(a_j - e_j.s)}{\prod_{j=1}^{q}\Gamma(b_j + c_j - c_j.s)\ \prod_{j=1}^{p}\Gamma(a_j - e_j + c_j.s)}\ x^{-s}\,ds \qquad (1\cdot1)$$

where $c_j > 0,\ j = 1, 2, \ldots, q,\ e_j > 0,\ j = 1, 2, \ldots, p,\ q \geqslant p + 1$ and all the poles of the integrand in (1·1) are simple.

He has also pointed out that it is most general function which needs further study.

Following Gupta (5, p. 98) we shall define this function, with slight difference in the parameters, in the form : (1·2)

$$H^{\,m,\,n}_{\,p,\,q}\left[\,x\,\middle|\,\begin{matrix}(a_p, e_p)\\(b_q, f_q)\end{matrix}\,\right] \equiv H^{\,m,\,n}_{\,p,\,q}\left[\,x\,\middle|\,\begin{matrix}(a_1, e_1), (a_2\, e_2), \ldots, (a_p, e_p)\\(b_1, f_1), (b_2, f_2), \ldots, (b_q, f_q)\end{matrix}\,\right]$$

$$= \frac{1}{\pi i}\int_L \frac{\prod_{j=1}^{m}\Gamma(b_j - f_j.s)\ \prod_{j=1}^{n}\Gamma(1 - a_j + e_j.s)}{\prod_{j=m+1}^{q}\Gamma(1 - b_j + f_j.s)\ \prod_{j=n+1}^{p}\Gamma(a_j - e_j.s)}\,x^{s}\,ds$$

where L, is a suitable contour of Barnes type such that the poles of $\Gamma(b_j - f_j s)$, $j = 1, 2, \ldots, m$, lie on the right and those of $\Gamma(1 - a_j + e_j s)$, $j = 1, 2, \ldots n$, on the left of the contour. An empty product is to be interpreted as 1, $0 \leqslant n \leqslant p$, e's and f's are all positive. Also the parameters are so restricted that the integral on the right of (1·2) is convergent.

The object of this note is to obtain two theorems on H-Functions. Theorem I is an "Addition Theorem" on H-Function. The result on G-Function by Edelstein (4) follows as an immediate consequence of this theorem. In Theorem II, we evaluate an integral involving product of two H-Functions. Since H-Function is more general than even Meijer's G-Function, the result obtained here becomes a master or key formula from which a large number of relations can be deduced for functions appearing in applied Mathematics and Mathematical Physics.

The following special cases of H-Function are worthy of note :

$$H\begin{matrix}m, n\\ p, q\end{matrix}\left[x \,\middle|\, \begin{matrix}(a_1, c), (a_2, c), \ldots, (a_p, c)\\ (b_1, c), (b_2, c), \ldots, (b_q, c)\end{matrix}\right] = \frac{1}{c}\, G\begin{matrix}m, n\\ p, q\end{matrix}\left(x^{1/c} \,\middle|\, \begin{matrix}a_1, a_2, \ldots, a_p\\ b_1, b_2, \ldots, b_q\end{matrix}\right) \tag{1·3}$$

$$H\begin{matrix}2, 0\\ 0, 2\end{matrix}\left[x \,\middle|\, \left(\frac{l}{2} + \tfrac{1}{4} + \frac{\nu}{2}, \tfrac{1}{2}\right), \left(\frac{l}{2} + \tfrac{1}{4} - \frac{\nu}{2}, \tfrac{1}{2}\right)\right] = 4 \cdot x^{l+\frac{1}{2}} K_\nu(2x) \tag{1·4}$$

$$H\begin{matrix}2, 0\\ 1, 2\end{matrix}\left[x \,\middle|\, \begin{matrix}(l - 2k, 1)\\ (l - k + m, 1), (l - k - m, 1)\end{matrix}\right] = x^{l-k-\frac{1}{2}} \cdot e^{-\frac{1}{2}x} \cdot W_{k+\frac{1}{2}, m}(x) \tag{1·5}$$

$$H\begin{matrix}1, 0\\ 0, 2\end{matrix}\left[x \,\middle|\, \left(\tfrac{1}{4} + \frac{\nu}{2}, \tfrac{1}{2}\right), \left(\tfrac{1}{4} - \frac{\nu}{2}, \tfrac{1}{2}\right)\right] = 2\, x^{\frac{1}{2}} J_\nu(2x) \tag{1·6}$$

$$H\begin{matrix}1, 0\\ 0, 1\end{matrix}\left[x \,\middle|\, (0, 1)\right] = e^{-x} \tag{1·7}$$

$$H\begin{matrix}1, 0\\ 0, 2\end{matrix}\left[x \,\middle|\, (0, \tfrac{1}{2}), (\tfrac{1}{2}, \tfrac{1}{2})\right] = \frac{2}{\sqrt{\pi}} \cos 2x \tag{1·8}$$

$$H\begin{matrix}1, 0\\ 0, 2\end{matrix}\left[x \,\middle|\, (\tfrac{1}{2}, \tfrac{1}{2}), (0, \tfrac{1}{2})\right] = \frac{2}{\sqrt{\pi}} \sin 2x \tag{1·9}$$

2. *Theorem I*

$$H\begin{matrix}m, n\\ p, q\end{matrix}\left[(x + y) \,\middle|\, \begin{matrix}(a_p, e_p)\\ (b_q, f_q)\end{matrix}\right] \tag{2·1}$$

$$= H\begin{matrix}m, n\\ p, q\end{matrix}\left[x \,\middle|\, \begin{matrix}(a_p, e_p)\\ (b_q, f_q)\end{matrix}\right] + \sum_{r=1}^{\infty} \left(\frac{y}{x}\right)^r \cdot \frac{1}{\lfloor r} \cdot H\begin{matrix}m, n+1\\ p+1, q+1\end{matrix}\left[x \,\middle|\, \begin{matrix}(0, 1), (a_p, e_p)\\ (b_q, f_q), (r, 1)\end{matrix}\right]$$

provided $\gamma = \sum_{j=1}^{m} (f_j) - \sum_{j=m+1}^{q} (f_j) + \sum_{j=1}^{n} (e_j) - \sum_{j=n+1}^{p} (e_j) > 0$,

$$|\arg(x + y)| < \tfrac{1}{2}\gamma\pi, \quad |\arg(x)| < \tfrac{1}{2}\gamma\pi, \quad \left|\frac{y}{x}\right| < 1, \tag{A}$$

and the series on the right is convergent.

Proof: We have

$$H\begin{matrix} m, n \\ p, q \end{matrix}\left[(x+y) \,\middle|\, \begin{matrix} (a_p, e_p) \\ (b_q, f_q) \end{matrix} \right]$$

$$= \frac{1}{2\pi i}\int_L \frac{\prod_{j=1}^{m}\Gamma(b_j - f_j.s)\ \prod_{j=1}^{n}\Gamma(1-a_j+e_j.s)}{\prod_{j=m+1}^{q}\Gamma(1-b_j+f_j.s)\ \prod_{j=n+1}^{p}\Gamma(a_j-e_j.s)}(x+y)^s\,ds$$

$$= \frac{1}{2\pi i}\int_L \frac{\prod_{j=1}^{m}\Gamma(b_j - f_j.s)\ \prod_{j=1}^{n}\Gamma(1-a_j+e_j.s)}{\prod_{j=m+1}^{q}\Gamma(1-b_j+f_j.s)\ \prod_{j=n+1}^{p}\Gamma(a_j-e_j.s)} x^s \cdot \left[1 + \sum_{r=1}^{\infty}\left(\frac{y}{x}\right)^r \frac{(-1)^r(-s)^r}{\lfloor r}\right] ds$$

provided $\left|\frac{y}{x}\right| < 1$

Now $$(-1)^r(-s)_r = \frac{\Gamma(1+s)}{\Gamma(1+s-r)}$$

So we get

$$H\begin{matrix} m, n \\ p, q \end{matrix}\left[(x+y) \,\middle|\, \begin{matrix} (a_p, e_p) \\ (b_q, f_q) \end{matrix} \right]$$

$$= H\begin{matrix} m, n \\ p, q \end{matrix}\left[x \,\middle|\, \begin{matrix} (a_p, e_p) \\ (b_q, f_q) \end{matrix} \right] +$$

$$+ \frac{1}{2\pi i}\sum_{r=1}^{\infty}\left(\frac{y}{x}\right)^r \frac{1}{\lfloor r}\int_L \frac{\prod_{j=1}^{m}\Gamma(b_j - f_j.s)\ \prod_{j=1}^{n}\Gamma(1-a_j+e_j.s)\,\Gamma(1+s)\,x^s\,ds}{\prod_{j=m+1}^{q}\Gamma(1-b_j+f_j.s)\,\Gamma(1-r+s)\ \prod_{j=n+1}^{p}\Gamma(a_j-e_j.s)}$$

$$= H\begin{matrix} m, n \\ p, q \end{matrix}\left[x \,\middle|\, \begin{matrix} (a_p, e_p) \\ (b_q, f_q) \end{matrix} \right] + \sum_{r=1}^{\infty}\left(\frac{y}{x}\right)^r \cdot \frac{1}{\lfloor r} \cdot H\begin{matrix} m, n+1 \\ p+1, q+1 \end{matrix}\left[x \,\middle|\, \begin{matrix} (0,1), (a_p, e_p) \\ (b_q, f_q), (r, 1) \end{matrix} \right]$$

It is easy to see that the term by term integration is valid as it does not involve the argument y/x and conditions (A) justify the existence of every H-function in the series. Moreover the series $\sum \frac{(-1)^r(-s)_r}{\lfloor r}(y/x)^r$ is uniformly convergent as long as $|y/x| < 1$ (1, p. 68 art. 2.1.6).

Putting $e_1 = e_2 = \ldots = e_p = 1 = f_1 = f_2 = \ldots = f_q$ we obtain Edelstein's result (4) which has been used by him in molecular quantum mechanics.

3. *Theorem II*

If $$x^{c-1}H\begin{matrix} m, n \\ p, q \end{matrix}\left[\alpha x^{\sigma} \,\middle|\, \begin{matrix} (a_p, e_p) \\ (b_q, f_q) \end{matrix} \right] \in L(0, \infty)$$

and $$M\left\{ H\begin{matrix} k, l \\ r, t \end{matrix}\left[\beta x^{\lambda} \,\middle|\, \begin{matrix} (c_r, h_r) \\ (d_t, u_t) \end{matrix} \right] ; 1-s \right\} \in L(-\infty, \infty)$$

where $s = c + i\tau$ and $M\{f(x); s\}$ denotes the Mellin Transform of $f(x)$, then

$$\int_0^{\infty} H\begin{matrix} m, n \\ p, q \end{matrix}\left[\alpha x^{\sigma} \,\middle|\, \begin{matrix} (a_p, e_p) \\ (b_q, f_q) \end{matrix} \right] \cdot H\begin{matrix} k, l \\ r, t \end{matrix}\left[\beta x^{\lambda} \,\middle|\, \begin{matrix} (c_r, h_r) \\ (d_t, u_t) \end{matrix} \right] dx$$

$$= \frac{1}{\sigma\lambda\,(\beta)^{1/\lambda}}\, H^{\,l+m,\ n+k}_{\,p+t,\ q+r}\left\{\frac{\alpha^{1/\sigma}}{3^{1/\lambda}}\middle|\begin{matrix}\left(a_1,\frac{e_1}{\sigma}\right),\ldots,\left(a_n,\frac{e_n}{\sigma}\right),\left(1-d_1-\frac{u_1}{\lambda},\frac{u_1}{\lambda}\right),\ldots\\ \left(1-d_t-\frac{u_t}{\lambda},\frac{u_t}{\lambda}\right)\left(a_{n+1},\frac{e_{n+1}}{\sigma}\right),\ldots,\left(a_p,\frac{e_p}{\sigma}\right)\\ \left(b_1,\frac{f_1}{\sigma}\right),\ldots,\left(b_m,\frac{f_m}{\sigma}\right),\left(1-c_1-\frac{h_1}{\lambda},\frac{h_1}{\lambda}\right),\ldots\\ \left(1-c_r-\frac{h_r}{\lambda},\frac{h_r}{\lambda}\right),\ b_{m+1},\left(\frac{f_{m+1}}{\lambda}\right),\ldots,\left(b_q,\frac{f_q}{\sigma}\right)\end{matrix}\right\} \quad (3\cdot1)$$

provided that $\sigma > 0$, $\lambda > 0$, and the conditions (i), (ii) along with one of the conditions in (iii) and (iv) given below are satisfied.

$$(i) \quad -\sigma \min_{1\leqslant j\leqslant m} R\left(\frac{b_j}{f_j}\right) < R(s) < \frac{\sigma}{e_j} - \sigma \max_{1\leqslant j\leqslant n} R\left(\frac{a_j}{e_j}\right),$$

$$-\lambda \min_{1\leqslant j\leqslant k} R\left(\frac{d_j}{u_j}\right) < R(s) < \frac{\lambda}{h_j} - \lambda \max_{1\leqslant j\leqslant l} R\left(\frac{c_j}{h_j}\right).$$

$$(ii) \quad \lambda \min_{1\leqslant j\leqslant k} R\left(\frac{d_j}{u_j}\right) + \sigma \min_{1\leqslant j\leqslant m} R\left(\frac{b_j}{f_j}\right) + 1 \geqslant 0,$$

$$\left[\frac{1-\max R(a_j)}{e_j}\right]_{1\leqslant j\leqslant n} + \lambda\left[\frac{1-\max R(c_j)}{h_j}\right]_{1\leqslant j\leqslant l} > 1$$

$$(iii) \quad \gamma > 0,\ |\arg(\alpha)| > \tfrac{1}{2}\gamma\pi$$

or

$$\gamma \geqslant 0,\ |\arg(\alpha)| \leqslant \tfrac{1}{2}\gamma\pi \text{ and } R(\delta+1) < 0,$$

$$R\left(\delta+\delta'+1-\frac{1}{\lambda}\sum_{1}^{r} h_j + \frac{1}{\lambda}\sum_{1}^{t} u_j,\right) < 0,$$

$$(iv) \quad \gamma' > 0,\ |\arg(\beta)| < \tfrac{1}{2}\gamma'\pi$$

or

$$\gamma' \geqslant 0,\ |\arg(\beta)| \leqslant \tfrac{1}{2}\gamma'\pi \text{ and } R(\delta'+1) < 0,$$

$$R\left(+\delta'+1-\frac{1}{\lambda}\sum_{1}^{r} h_j + \frac{1}{\lambda}\sum_{1}^{t} u_j\right) < 0,$$

where

$$(v) \quad \begin{cases} \gamma = \sum_{j=1}^{n}(e_j) - \sum_{j=n+1}^{p}(e_j) + \sum_{j=1}^{m}(f_j) - \sum_{j=m+1}^{q}(f_j) \\ \gamma' = \sum_{j=1}^{l}(h_j) - \sum_{j=l+1}^{r}(h_j) + \sum_{j=1}^{k}(u_j) - \sum_{i=k+1}^{t}(u_j) \\ \delta = \tfrac{1}{2}(p-q) + \sum_{j=1}^{q}(b_j) - \sum_{j=1}^{p}(a_j) \\ \delta' = \tfrac{1}{2}(r-t) + \sum_{j=1}^{t}(d_j) - \sum_{j=1}^{r}(c_j) \end{cases}$$

Proof: If $F(s) = M\{f(x), s\}$ and $G(s) = M\{g(x); s\}$ denote the Me Transforms of $f(x)$ and $g(x)$ respectively, then by Faltung Theorem (6, p. 43)

$$(A) \qquad \int_0^\infty f(x).\, g(x)\, dx = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} F(s)\, G(1-s)\, ds$$

provided $x^{c-1} f(x)$ belongs to $L(0, \infty)$ and $G(1 - c - ir)$ belongs to $L(-\infty, \infty)$; $s = c + ir$

Now
$$M\left\{ H^{\,d,\,e}_{u,\,v}\left[\mu x^{\nu} \,\middle|\, \begin{matrix}(a_u, \eta_u)\\ (\beta, \rho_v)\end{matrix} \right]; s\right\}$$

$$= \frac{1}{\nu} \cdot \frac{\prod_{j=1}^{d} \Gamma\left(\beta_j + \frac{\rho_j}{\nu}\cdot\right) \prod_{j=1}^{e} \Gamma\left(1 - a_j - \frac{\eta_j}{\nu}\cdot s\right)}{\prod_{j=d+}^{u} \Gamma\left(1 - \beta_j - \frac{\rho_j}{\nu}\cdot s\right) \prod_{j=e+1}^{u} \Gamma\left(a_j + \frac{\eta_j}{\nu}\cdot s\right)} \mu^{\frac{-s}{\nu}}$$

provided

$$(a) \qquad -\min_{1 \leqslant j \leqslant d} R\left(\frac{\beta_j}{\rho_j}\right) < R(s) < \frac{\nu}{\eta_j} - \nu \max_{1 \leqslant j \leqslant e} R\left(\frac{a_j}{\eta_j}\right)$$

and

$$(\beta) \qquad \left[\begin{matrix} \theta > 0, & |\arg(\mu)| < \frac{1}{2}\theta\pi \\ \theta \geqslant 0, & |\arg(\mu)| \leqslant \frac{1}{2}\theta\pi \text{ and } R(\phi + 1) < 0, \end{matrix} \right.$$

or

where

$$\theta = \sum_{j=1}^{e} (\eta_j) - \sum_{j=e+1}^{u} (\eta_j) + \sum_{j=1}^{d} (\rho_j) - \sum_{j=d+1}^{v} (\rho_j)$$

$$\phi = \tfrac{1}{2}(u - v) + \sum_{j=1}^{v} (\beta_j) - \sum_{j=1}^{u} (a_j)$$

Using this to find the Mellin Transforms of

$$H^{\,m,\,n}_{p,\,q}\left[\alpha x^{\sigma} \,\middle|\, \begin{matrix}(a_p, e_\rho)\\ (b_q, f_q)\end{matrix} \right] \text{ and } H^{\,k,\,l}_{r,\,t}\left[\beta x^{\lambda} \,\middle|\, \begin{matrix}(c_r, h_r)\\ (d_t, u_t)\end{matrix} \right]$$

we apply Theorem (A) above and interpret the right-hand side by means of (1·2) to get the desired result under conditions stated.

Special Cases

Putting $\lambda = \sigma = 1$ and $e_1 = e_2 = \ldots = e_p = 1, f_1 = f_2 = \ldots = f_q = 1 = h_1 = h_2 = \ldots = h_r = u_1 = u_2 = \ldots = u_t$, then in view of (1·3) and (1 ; p. 209 (8), (9)), we have,

$$\int_0^\infty G^{\,m,\,n}_{p,\,q}\left(\alpha x \,\middle|\, \begin{matrix} a_1, a_2, \ldots, a_p \\ b_1, b_2, \ldots, b_q \end{matrix} \right) G^{\,k,\,l}_{r,\,t}\left(\beta x \,\middle|\, \begin{matrix} c_1, c_2, \ldots, c_r \\ d_1, d_2, \ldots, d_t \end{matrix} \right) dx$$

$$= \frac{1}{\alpha}\, G^{\,n+k,\,l+m}_{q+r,\,p+t}\left(\frac{\beta}{\alpha} \,\middle|\, \begin{matrix} -b_1, \ldots, -b_m, c_1, \ldots, c_r, -b_{m+1}, \ldots, -b_q \\ -a_1, \ldots, -a_n, d_1, \ldots, d_t, -a_{n+1}, \ldots, -a_p \end{matrix} \right)$$

under relevant conditions. This is a known result (2 ; p. 422).

If further we put

$$(a) \qquad k = 2 = t,\ l = 0 = r,\ \lambda = 1, \beta = \frac{u}{2},\ u_1 = \tfrac{1}{2} = u_2$$

$$d_1 = \frac{l_1}{2} + \tfrac{1}{4} + \frac{\nu}{2},\ d_2 = \frac{l_1}{2} + \tfrac{1}{4} - \frac{\nu}{2}$$

and

$$(b) \quad k = 2 = t,\ l = 0,\ r = 1,\ \lambda = 1,\ \beta = u,\ h_1 = 1 = u_1 = u_2$$
$$c_1 = l_1 - 2k_1,\ d_1 = l_1 - k_1 + r_1,\ d_2 = l_1 - k_1 - r_1$$

in (3·1), then by virtue of (1·4) and (1·5) we get the results obtained by Gupta (5 ; p. 99 (6) and (7)) viz ;

$$\int_0^\infty x^{l_1} \cdot H^{m,n}_{p,q}\left[\alpha x^\sigma \,\middle|\, \begin{matrix}(a_p, e_p)\\(b_q, f_q)\end{matrix}\right] (ux)^{\frac{1}{2}} K_\nu(ux)\, dx \qquad (3\cdot2)$$

$$= u^{-l_1-1} \cdot 2^{l_1-\frac{1}{2}} \cdot H^{m,n+2}_{p+2,q}\left[a \cdot \left(\frac{2}{u}\right)^\sigma \,\middle|\, \begin{matrix}\left(\frac{1}{4} - \frac{l_1}{2} - \frac{\nu}{2}, \frac{\sigma}{2}\right), \left(\frac{1}{4} - \frac{l_1}{2} + \frac{\nu}{2}, \frac{\sigma}{2}\right), (a_1, e_1), \ldots, (a_p, e_p)\\ (b_1, f_1), \ldots, (b_q, f_q)\end{matrix}\right] \qquad (3\cdot2)$$

and

$$\int_0^\infty (ux)^{-k_1-\frac{1}{2}} e^{-\frac{1}{2}ux} \cdot W_{k_1+\frac{1}{2}, r_1}(ux) \cdot x^{l_1} \cdot H^{m,n}_{p,q}\left[\alpha x^\sigma \,\middle|\, \begin{matrix}(a_p, e_p)\\(b_q, f_q)\end{matrix}\right] dx$$

$$= u^{-l_1-1} \cdot H^{m,n+2}_{p+2,q+1}\left[\frac{\alpha}{u^\sigma} \,\middle|\, \begin{matrix}(k_1 - r_1 - l_1, \sigma), (k_1 + r_1 - l_1, \sigma), (a_1, e_1), \ldots, (a_p, e_p)\\ (b_1, f_1), \ldots, (b_q, f_q), (2k_1 - l_1, \sigma)\end{matrix}\right] \qquad (3\cdot3)$$

respectively with necessary conditions stated therein.

It is interesting to observe that in view of the relations (1·6), (1·7), (1·8) and (1·9), the results on Hankel, Laplace and the Fourier Transforms become particular cases of our result.

Acknowledgements

The author is extremely grateful to Dr. C. B. L. Verma who very kindly suggested the problem and took keen interest in the preparation of this note. Thanks are also due to the referee for his valuable suggestions.

References

1. Bateman Manuscript Project. Higher Transcendental Functions Vol. 1 (1953.)
2. Bateman Manuscript Project. Tables of Integral Transforms Vol. 2 (1954.)
3. Fox, Charles. *Trans. Amer. Math. Soc.*, **98** : (1961) 395-429,.
4. Edelstein, L. A. *Proc. Cambridge Phil. Soc.*, **60** : (196 .) : 533-538.
5. Gupta, K. C. Annales de la Societe Scientifique de Bruxelles T. **79 II** : (1965) 97-106.
6. Sneddon, I. N. Fourier Transforms. McGraw-Hill Book Company (1951).

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968

Basic slag, a fertilizer for acid soils

By

S. C. MANDAL, K. K. JHA *and* H. SINHA

Agricultural Research Institute, Kanke

In recent years, the importance of basic slag in increasing crop production and improving fertility of soils has been emphasized, time and again, by Dhar (1955, 1961, 1962 and 1964). The investigations of Dhar (1962) and Ghosh (1963) showed that the beneficial effects of basic slag on the yield of paddy were comparable to those of superhosphate in normal soils where as in the poor and acid soils basic slag was superior to superphosphate, when used either alone or in combination with organic matter. Ghosh (1965) and Tamboli (1966) have also found beneficial effects of basic slag in the acid soils of Orissa and Madhya Pradesh respectively. In the plateau region of Bihar the upland soils covering about three million acres are acidic in reaction. These soils are poor in phosphate and they respond to lime (Mandal *et al*, 1966). Basic slag contains considerable quantities of lime and threfore it can be used as a liming material. The phosphate contents of Indian basic slags are, generally, not very high (2 – 4%) except that obtained from the Dupleix furnace of the Tata Steel Factory (7–8% P_2O_5). Yet, the basic slag has great potentiality of meeting the phosphate needs of a considerable fraction of our acid soils. Since the big steel factories of the country are located either in Bihar or in its neighbourhood the utilization of basic slag as a fertilizing material for the acid soils of Bihar merits consideration. With the objective of finding out the manurial value of basic slag on investigation was undertaken at the Agricultural Research Institute, Kanke. After pilot trials for three years (1958–61) in pots and micro-plots, with success, the experiment was transferred to the field to determine crop response, more correctly.

Experimental

Basic slag, containing 7·24% P_2O_5,, 43·2% CaO and 6·87% MgO, obtained from Tata Iron and Steel Company was used in the investigation. It was compared against other phosphatic fertilizers *viz*. superphosphate, rock phosphate, bonemeal, dicalcium phosphate and glycerophosphate. The experiment was conducted at the Kanke farm on an acidic red loam soil with pH 5·3. It was laid out in a randomized block design with five replications and was carried out for three years without any change of design or treatments. Pea was selected as the experimental crop. The experiment was laid out in two series : (1) Limed and (2) Unlimed. In the lime series the soil was limed @ 4000 lbs per acre, on the basis of lime requirement studies on this soil carried out in earlier years (Sinha *et al*, 1955). The field was uniformly manured with 10 lb N, 40 lb P_2O_5 and 40 lb K_2O per acre.

Analyses of soil samples collected after the harvest of the peas were carried on for pH, exchangeable calcium and available phosphate. The pH was determined in Beckman's pH meter using glass electrodes and the exchangeable calcium in the ammonium acetate leachate of the soil following the procedure described by

Jackson (1958). Available phosphate was estimated colorimetrically as Bray's p_1 values, (Bray and Kurtz, 1945) which have been found to correlate well with crop response and considered suitable for the acid soil tracts of the State (Rai, Prasad and Mandal 1963).

Results and Discussion

Yield of peas obtained in this experiment during the years 1961–64 are given in Table I.

TABLE I

Comparative effects of basic slag and other phosphates on the grain yield of peas
(Mds/acre)

Phosphate used	Without lime			With lime		
	1961-62	1962-63	1963-64	1961-62	1962-63	1963-64
None	3·0	0·8	0·2	7·9	5·5	3·7
Superphosphate	5·8	2·8	0·9	14·1	15·6	10·0
Rock Phosphate	3·8	2·3	0·4	10·2	9·9	5·6
Bone meal	5·4	3·6	0·5	10·7	9·4	6·3
Dicalcium phosphate	5·7	2·5	0·6	13·6	11·9	6·3
Glycerophosphate	4·2	2·1	0·5	16·4	8·4	4·1
Basic slag	8·1	5·8	7·6	9·9	11·4	10·5
C. D at 5%	1·5	2·1	0·7	3·8	2·4	2·1

From the results recorded in the above table it appears that in the absence of liming basic slag was the best phosphatic fertilizer in all the years showing its remarkable superiority over the standard phpsphatic fertilizer, *viz.*, superphosphate. These results, therefore, do not support the view commonly held by many of our Agronomists, inspite of well known effects of rock phosphates, basic slag etc. in acid soils in the west, that superphosphate is always superior to other phosphatic fertilizers. On liming the acid soil, however, superphosphate was found to be superior to basic slag in the first two years but the effects levelled up in the third year. In the first year of the experiment dicalcium phosphate and glycerophosphate were also more effective than the basic slag in the limed soil, but not in subsequent years. These results suggest that the cumulative effect of the basic slag is highly beneficial.

Soil analysis data of the after-harvest samples (1963-64) are given in Table II.

TABLE II

Effects of basic slag and other phosphates on pH, available phosphate and exchangeable calcium

Phosphate added	Without lime			With lime		
	pH	Exch. Ca (m. e. %)	Available P (p.p.m.)	pH	Exch. Ca (m. e. %)	Available P(p.p.m.)
None	5·2	2·6	8	6·2	5·3	14
Superphosphate	5·0	3·2	45	6·3	5·8	45
Rock phosphate	5·6	3·6	33	6·4	5·8	17
Bone meal	5·4	2·9	29	6·6	6·2	18
Dicalcium phosphate	5·1	2·4	28	6·4	5·7	21
Calcium Glycero-phosphate	4·9	1·3	26	6·6	5·7	24
Basic slag	6·4	5·6	30	7·0	7·9	26

The soil analysis data in Table II suggest that the crop response to basic slag may be, to a great extent, due to its acid neutralising action resulting from its high contents of Ca and Mg. Even without liming the basic slag treated subplot had a pH of 6·4 as a result of slag application for three years compared to 4·9 to 5·6 in other treatments. In the limed plot, the pH varied from 6·2 to 6·6 in subplots treated with phosphatic carriers other than basic slag, while the pH was 7·0 in the basic slag treated subplots after three years of continuous application. Consistent with the pH values, basic slag treated subplots, invariably, showed higher exchangeable calcium compared to those treated with other phosphates.

The neutralisation of soil acidity alone, however, could not account wholly for the crop response to basic slag which must be partly also due to the supply of phosphate. That raising of pH leads to higher uptake of phosphate by plants in these soils, has been shown by Rai, Prasad and Mandal (1963). The possibility of crop response resulting from the micronutrient contents of basic slag is discounted here, since no response to any micronutrient, except molybdenum, has been observed in these soils in the past (1957-59). Moreover, this soil has been found to be rich in some micronutrients, *e.g.*, Fe and Mn.

Bray's P_1 values, however, do not correspond to the response of peas to superphosphate and basic slag applications. The same was observed by Rai, Prasad and Mandal (1963) who found that the uptake of phosphate by plants correlated more with liming of acid soil than available soil phosphate as indicated by Bray's P_1 values, even though these values have been found to be more reliable indices of available phosphate status of soils than other values, *e. g.* Olsen's, Truog's, Egner's, Williams', Dyer's etc.

Crop response to basic slag application, thus, offers, the possibility of its use as a dual purpose fertilizer for the amelioration of soil acidity as well as for supplying phosphate to plants, specially the legumes. The total amount of basic slag produced annually as a waste-product of the steel factories in the country is estimated at about 7 lakh tons which is likely to go up to 1 million tons very soon. The lime content of basic slag, in terms of CaO and MgO is nearly 50%. Thus, in basic slag produced at present, we have a potential lime source of five lakh tons.

On an average, the lime requirement of acid soils in Chotanagpur, where two steel plants are located and three are in close proximity, has been estimated at one ton per acre, once in 4 years. The basic slag produced in the country can meet the lime requirement of 2·5 million acres of acid soils and at the same time supply 30,000 tons of P_2O_5 annually, sufficient to meet the requirement of about 1·5 million acres.

Summary

Three years of field trials on peas in an acidic red loam soil of Chotanagpur in Bihar have shown the possibility of the utilization of basic slag as a soil amendment and a source of phosphate at relatively small cost. It will also provide solution to the problem of its disposal from factory premises and stop its misuse as a road building material, in a country facing acute fertilizer shortage at the moment.

Acknowledgements

The authors greatfully acknowledge the kind advice and encouragement given by Dr. S. Ramanujam, Ex-Director of Agricultural Research, Bihar during the course of this investigation. They also express their sincere thanks to Chief Chemist, Tata Iron and Steel Company for providing the slag for field experiments.

References

Agricultural Research Institute, Kanke. *Annual Reports*, 1957–59.

Bray, R. H. Kurtz, L. T. *Soil Sc.*, **59** : 39, 1945.

Dhar, N. R. *Proc. Nat. Acad. Sci. India*, **A24**(*i*) : 5, 1955.

Dhar, N. R. *General Presidential address, 48th session, Indian Science Congress Asssciation, Roorkee*, 1961.

Dhar, N. R. *J. Indian Soc. Soil Sci.*, **10** : 75, 1962.

Dhar, N. R. *Bull. Nat. Inst. Sci. India*, No. 26, 1964.

Ghosh, P. C. *Proc. Ind. Sc. Congr. Abstracts*, 1965.

Ghosh, S. K. *J. Indian Soc. Soil Sci.*, **11** ; 116, 1963.

Jackson, M. L. *Soil Chemical Analysis*, Constable and Co. U. S. A., 1958.

Mandal, S. C., Sinha, H. Prasad, C. R. and Ali, M. A. *J. Ind. Soc. Soil Sci.*, **14** : 127, 1966.

Rai, A. K., Prasad, C. R. and Mandal, S. C. *Jr. Ind. Soc. Soil Sci.*, **11** : 137-140, 1963.

Sinha, H., Ali, M. A. and Mandal, S. C. *Indian Agriculturist*, **9** : 157, 1965.

Tamboli, P. M. *Soil Sci. Comm. ICAR. Proc.* (*Mimeographed*), 1966.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968.

On Integro-Exponential Transform

By

R. N. PANDEY & R. L. BARANWAL

College of Technology, Banaras Hindu University

[Received on 29th November, 1966]

Abstract

In this paper, a new generalisation of the Laplace transform has been defined in which the kernel of the transform contains integro-exponential function

$$E_\mu(x) = e^{-x} \int_0^\infty e^{-xy} (1+y)^{-\mu}\, dy,\ 0 \leqslant Re(\mu) < 1$$

defined by Busbridge, I. W. [1(*a*)]. A few infinite integrals involving Meijer's *G*-function, MacRobert's *E*-function, Hypergeometric function etc. have been evaluated with the help of this transform.

1. A function $\psi(p)$ is said to be the Laplace transform of $f(t)$ if

$$\psi(p) = p \int_0^\infty e^{-pt} f(t)\, dt. \tag{1·1}$$

Dr. R. S. Varma gave a generalisation of (1·1) in the form

$$\phi(p) = p \int_0^\infty e^{-\frac{1}{2}pt} (pt)^{m-\frac{1}{2}} W_{k,m}(pt) f(t)\, dt. \tag{1·2}$$

Since

$$W_{-m+\frac{1}{2},m}(x) = x^{-m+\frac{1}{2}} e^{-\frac{1}{2}x} \tag{1·3}$$

(1·2) reduces to (1·1) when $k = -m + \frac{1}{2}$.

We define a transform known as Integro-Exponential transform [8], as

$$\phi(p) = p \int_0^\infty e^{-\mu px} (px)^\sigma E_\mu(px) f(x)\, dx = p \int_0^\infty K(p, x) f(x)\, dx, \tag{1·4}$$

with the proviso that $Re(\sigma + \delta_1 + 1) > 0$, $Re(\sigma + \mu + \delta_1) > 0$, $f(x) = 0\ (x^{\delta_1})$ for small x, $K(p_0, x) f(x)$ is bounded for $x \geqslant 0$, $Re(p) > Re(p_0) > 0$, $Re(a+1) > 0$ and $Re(\mu) \geqslant 0$.

$E_\mu(x)$ is the integro-exponential function defined by Busbridge, I. W. as

$$E_\mu(x) = e^{-x} \int_0^\infty e^{-xy} (1+y)^{-\mu}\, dy, \qquad Re(\mu) > 0.$$

We shall denote (1·1), (1·2) and (1·4) symbolically as

$$\psi(p) \subset f(t), \qquad \phi(p) \overset{V}{\underset{k,m}{\rightleftharpoons}} f(t)$$

and

$$\phi(p) \underset{\mu,a}{\overset{\sigma}{\rightarrow}} f(x) \text{ respectively.}$$

In this paper we have attempted to prove a theorem for the transform (1·4) and to evaluate some infinite integrals by making use of that theorem.

2. *Theorem* 1. If

$$\psi\left(\frac{1}{p}\right) \supset f(t)$$

and

$$\phi(p) \xrightarrow[o,\ \mu]{1-\mu} t^{-1} e^{-b/t}\, \psi(t),$$

then

$$\phi(p) = 2p^{\frac{3}{2}-\frac{1}{2}\mu} \int_0^\infty \frac{K_{1-\mu}\left[2\sqrt{p(t+b)}\right]}{(t+b)^{\frac{1}{2}(\mu+1)}} f(t)\, dt, \tag{2·1}$$

provided the integral converges and $Re(p) > 0$, $Re(b) > 0$ and $Re(\mu) > 0$.

Proof: We have

$$\psi\left(\frac{1}{p}\right) \subset f(t).$$

Also expanding

$$E_\mu(x) = e^{-x} \int_0^\infty e^{-xy} (1+y)^{-\mu}\, dy$$

as

$$E_\mu(x) = x^{\mu-1}\Gamma(1-\mu) - \sum_{k=0}^{\infty} \frac{(-1)^k x^k}{(k-\mu+1)\,\lfloor k}, \quad 0 \leqslant Re(\mu) < 1$$

and integrating term by term, which is justifiable, we get

$$t^{\frac{1}{2}\mu} e^{-bt} \left(\frac{a}{t}\right)^{1-\frac{1}{2}\mu} E_\mu\left(\frac{a}{t}\right) \supset 2a^{\frac{1}{2}}\, p(p+b)^{-\frac{1}{2}-\frac{1}{2}\mu} K_{1-\mu}\left[2\sqrt{(p+b)a}\right], \tag{2·2}$$

where $Re(a) > 0$, $Re(b) > 0$, $Re(p) > 0$ and $Re(\mu) > 0$.

Now using the relations in Parseval's formula that if

$$\phi_1(p) \subset f_1(t) \qquad \text{and} \qquad \phi_2(p) \supset f_2(t)$$

then

$$\int_0^\infty \frac{\phi_1(t)\, f_2(t)}{t}\, dt = \int_0^\infty \frac{\phi_2(t)\, f_1(t)}{t}\, dt, \tag{2·3}$$

we find that

$$\int_0^\infty a^{1-\frac{1}{2}\mu}\, t^{\mu-2}\, e^{-bt} E_\mu\left(\frac{a}{t}\right) \psi\left(\frac{1}{t}\right) dt = 2a^{\frac{1}{2}} \int_0^\infty \frac{K_{1-\mu}\left[2\sqrt{a(x+b)}\right]}{(x+b)^{\frac{1}{2}(\mu+1)}} f(x)\, dx. \tag{2·4}$$

Here replacing t by $\frac{1}{t}$ and a by p, we obtain

$$p \int_0^\infty e^{-b/t} (pt)^{-\mu} E_\mu(pt)\, \psi(t)\, dt = 2p^{\frac{1}{2}-\frac{1}{2}\mu} \int_0^\infty \frac{K_{1-\mu}\left[2\sqrt{p(x+b)}\right]}{(x+b)^{\frac{1}{2}(\mu+1)}} f(x)\, dx. \tag{2·5}$$

Corollary.—On putting $\mu = 0$ in the above theorem we have the following result of Tiwari, N. D.[9], *i.e.*

if

$$\psi\left(\frac{1}{p}\right) \supset f(t)$$

and

$$\phi(p) \supset t^{-1}\, e^{-b/t}\, \psi(t),$$

then

$$\phi(p) = 2\, p^{\frac{1}{2}} \int_0^\infty (t+b)^{-\frac{1}{2}}\, K[2\sqrt{p(t+b)}]\, f(t)\, dt \qquad (2{\cdot}6)$$

provided the integral exists.

3. *Example* 1. Expanding $E_\mu(x)$ as in (2·2) and integrating term by term, which is justifiable, we get

$$\int_0^\infty x^{\rho-1}\, e^{-\frac{1}{2}b/x} \left(\frac{x}{a}\right)^{1-\frac{1}{2}\mu} E_\mu\left(\frac{x}{a}\right)\, W_{\lambda,\nu}\left(\frac{b}{x}\right)\, dx$$

$$= b^\rho\, G^{4\,0}_{2\,4}\left(\frac{b}{a}\middle| \begin{matrix} 1+\frac{1}{2}\mu,\ 1-\lambda-t \\ 1-\frac{1}{2}\mu,\ \frac{1}{2}\mu,\ \frac{1}{2}+\nu-\rho,\ \frac{1}{2}-\nu-\rho \end{matrix}\right), \qquad (3{\cdot}1)$$

where

$Re(a) > 0$, $Re(b) > 0$, we find that

$$t^{-1}\, e^{-b/t}\, \psi(t) = t^{\rho-1}\, e^{-\frac{1}{2}b/t}\, W_{\lambda,\nu}\left(\frac{b}{t}\right)$$

$$\xrightarrow[0,\,\mu]{1-\mu} b^{\rho-\frac{1}{2}\mu}\, p^{1-\frac{1}{2}\mu} \times$$

$$\times\ G^{4\,0}_{2\,4}\left(bp\middle| \begin{matrix} 1+\frac{1}{2}\mu,\ -\lambda-\rho+\frac{1}{2}\mu \\ 1-\frac{1}{2}\mu,\ \frac{1}{2}\mu,\ \frac{1}{2}+\nu-\rho+\frac{1}{2}\mu,\ \frac{1}{2}-\nu-\rho+\frac{1}{2}\mu \end{matrix}\right)$$

$$= \phi(p), \qquad (3{\cdot}2)$$

and hence by Erdelyi[2] p. 294 (9), we get

$$\psi\left(\frac{1}{p}\right) = e^{\frac{1}{2}bp}\, p^{-\rho}\, W_{\lambda,\nu}(bp) \supset \frac{b^\lambda\, t^{\rho-\lambda}}{\Gamma(1-\frac{1}{2}\mu+\rho-\lambda)} \times$$

$$\times\ {}_2F_1\left[\begin{matrix} \frac{1}{2}-\lambda+\nu,\ \frac{1}{2}-\lambda-\nu \\ 1+\rho-\lambda \end{matrix};\ -\frac{t}{b}\right],$$

$$= f(t) \qquad (3{\cdot}3)$$

where $Re(1+\rho-\lambda) > 0$, $|\arg b| < \pi$.

On using the above values of $\phi(p)$ and $f(t)$, we get

$$2\int_0^\infty K_{1-\mu}\,[2\sqrt{p(t+b)}]\ {}_2F_1\left[\begin{matrix} \frac{1}{2}-\lambda+\nu,\ \frac{1}{2}-\lambda-\nu \\ 1+\rho-\lambda \end{matrix};\ -\frac{t}{b}\right] t^{\rho-\lambda}\, dt$$

$$= \Gamma(1+\rho-\lambda)\, b^{\rho-\frac{1}{2}\mu-\lambda}\, p^{-\frac{1}{2}}\, G^{4\,0}_{2\,4}\left(bp\middle| \begin{matrix} 1+\frac{1}{2}\mu,\ 2-\lambda-\rho+\frac{1}{2}\mu \\ 1-\frac{1}{2}\mu,\ \frac{1}{2}\mu,\ \frac{1}{2}+\nu-\rho+\frac{1}{2}\mu,\ \frac{1}{2}-\nu-\rho+\frac{1}{2}\mu \end{matrix}\right), \qquad (3{\cdot}4)$$

where $Re(1 + \rho - \lambda) > 0$, $Re(b) > 0$ and $Re(p) > 0$.

Example 2. Using the result of Gupta[4] (p. 134), we have

$$\psi\left(\frac{1}{p}\right) = p^{\frac{1}{2}-\frac{1}{2}\mu} e^{\frac{1}{2}bp} D_\mu(2\sqrt{bp})$$

$$\subset \frac{2^{\frac{1}{2}\mu} \cos[\mu \tan^{-1}\sqrt{t/b}]}{\sqrt{(\pi t)}\,(t+b)^{-\frac{1}{2}\mu}},$$

$$= f(t), \tag{3·5}$$

where $Re(b) > 0$, $Re(\mu) > 0$.

Now applying the theorem, we get

$$2\int_0^\infty t^{-\frac{1}{2}} (t+b)^{-\frac{1}{2}} K_{1-\mu}[2\sqrt{p(t+b)}] \cos(\mu \tan^{-1}\sqrt{t/b})\, dt$$

$$= \frac{\pi}{\sqrt{bp}} e^{\sqrt{bp}} (2\sqrt{bp})^{1-\frac{1}{2}\mu} E_\mu(2\sqrt{bp})\, W_{\frac{1}{2}\mu,\, \frac{1}{2}-\frac{1}{2}\mu}(2\sqrt{bp}) \tag{3·6}$$

where $Re(b) > 0$, $Re(\mu) > 0$.

Again on putting $\mu = 0$ in (3·6), we get

$$2\int_0^\infty t^{-\frac{1}{2}} (t+b)^{-\frac{1}{2}} [2\sqrt{p(t+b)}]\, dt$$

$$= 2\pi e^{\sqrt{bp}} E_0(2\sqrt{bp})\, W_{0,\frac{1}{2}}(2\sqrt{bp}), \tag{3·7}$$

where $Re(b) > 0$, $Re(p) > 0$.

Our thanks are due to Dr. G. Tripathi for his kind inspiration and help in the preparation of this paper.

References

1(*a*). Busbridge, I. W. *Quarterly Journal (Oxford Series)*, 176-84, 1950.

1(*b*). Erdelyi, A. *Higher Transcendental Functions*, Vol. I, 1953.

2. Erdelyi, A. *Table of Integral Transform*, Vol. 1, 1954.

3. Erdelyi, A. *Table of Integral Transforms*, Vol. 2, 1954.

4. Gupta, H. C. *Proc. Nat. Inst. Sci., India*, **24**(3) : 131, 1948.

5. Rathie, C. B. *Proc. Nat. Inst. Sci., India*, **20**(1) : 62, 1954

6. Rathie, C. B. *Proc. Nat. Inst. Sci., India*, **21A**(1) : 382, 1955.

7. Saksena, R. K. *Bull. Cal. Math. Soc.*, **53** : 155, 1961.

8. Pandey, R. N. Thesis for Ph. D. "on a Generalised Laplace Transform and Integro-Exponential Transform". *B. H. U.*, 1964.

9. Tiwari, N. D. *Scientific Research Jonrnal, B. H. U.*, 1943.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968

Theory of Plane Strain in Electrostrictive Dielectrics with an application to the bending of a clamped plate

By

GUNADHAR PARIA

Shri G vi idram Seksaria Technological Institute Indore (M. P.), India

[Received on 26th July, 1966]

Abstract

By developing the theory of plane strain in dielectric materials sensitive to electrostrictive effects, it is shown that the stress function and the electric potential satisfy two simultaneous differential equations which are highly non-linear. As an illustration of the theory, the bending of a plate clamped at one edge and loaded at the opposite edge is considered. The method of perturbation is used to solve the problem. An uncoupled solution is obtained as the first approximation and this is used for further approximations.

1. Introduction

Though there have been much experimental investigations [1, 2, 3] on the effect of electrostriction in dielectric solids, strictly mathematical formulation of the theory and the solutions of special problems based on such theory are very rare. Recently, Knops [4] has discussed reciprocal theorems of electrostriction by extending the Betti reciprocal theorem of the classical elasticity.

In the present paper we first formulate the theory of deformation of the electrostrictive dielectric solids in the sense of plane strain. By introducing the stress function and the electric potential function satisfy two simultaneous differential equations which are highly non-linear. This is a very wide departure from the classical theories of elasticity and electricity, where the stress function satisfies biharmonic equation and the electric potential function satisfies the harmonic equation independently of each other. To illustrate the theory we consider the bending of a plate which is clamped along one edge and possesses a mechanical load at the opposite edge. The electric potential is prescribed on one edge and other edges are kept at zero potentials. The method of purturbation is used to solve the problem. To the first approximation, an uncoupled solution is obtained and it is used for further approximations of the coupled solution. The purturbed effects on the stress function and the electric potential are obtained.

2. General theory of electrostrictive dielectrics

We consider an electrostrictive dielectric solid of which the elastic and electric properties are homogeneous and isotropic in the state of zero stress and zero strain. When the deformation is produced by the application of the electric field together with or without the mechanical forced, the electric properties may become anisotropic, and in such cases the coefficients of asisotropy depend upon the strains developed.

In this type of medium, the stress tensor σ_{ij} is related to the strain tensor e_{ij} and the etectric field E_i as [4(*ii*)]

$$\sigma_{ij} = \lambda e_{kk}\,\delta_{ij} + 2\mu\, e_{ij} + a\, E_i\, E_j + b\, E_m\, E_m\, \delta_{ij} \qquad (2{\cdot}1)$$

where λ and μ are Lame's elastic constants, while a and b are also constants describing the electrical properties of the dielectric. The symbol δ_{ij} represents the Kronecker delta.

The strains e_{ij} are expressed in terms of the mechanical displacement u_i by the usual formulae $e_{ij} = \frac{1}{2}(u_{ij} + u_{j,i})$. (2·2)

In the anisotropic medium the electrical displacement D_i is related to E_i as

$$D_i = K_{ij} E_j \tag{2·3}$$

where the anisotropic coefficients K_{ij} in the isothermal conditions are given by

$$k_{ij} = k\delta_{ij} + k_1 e_{ij} + k_2 e_{kk} \delta_{ij} \tag{2·4}$$

The constants K, K_1 and K_2 are characteristic of the electrostrictive property and are to be determined experimentally. It may be shown that [1,2] the constants a and b involved in relation (2·1) are expressible in terms of these quantities by

$$a = 2k - k_1, \qquad b = -(k_1 + k_2). \tag{2·5}$$

The equations of equilibrium of stresses are

$$\frac{\partial \sigma_{ij}}{\partial X_j} = 0, \tag{2·6}$$

and Maxwell's electrical equations are

$$\text{curl}\,\vec{E} = 0, \tag{2·7}$$

$$\text{div}\,\vec{D} = P_1. \tag{2·8}$$

These are satisfied irrespective of the properties of the medium. Here P_1 is the volume charge density in mks units.

Equations from (2·1) to (2·8) are the fundamental equations describing the deformations in an etectrostrictive dielectric. They are to be solved under prescribed electrical and mechanical boundary conditions. It is worth while to state here that these equations ultimately lead in general to complicated simultaneous non-linear equations.

3. Equations in plane strains

In problems involving plain strains we may assume

$$u_1 = u(x, y), \quad u_2 = v(x, y), \quad u_3 = 0 \tag{3·1}$$

and all functions depend upon x and y only. Then the relation 2·4) implies

$$\begin{aligned} k_{11} &= k + (k_1 + k_2) e_{11} + k_2 e_{22}, \\ k_{22} &= k + (k_1 + k_2) e_{22} + k_2 e_{11}, \\ k_{33} &= k + k_2 (e_{11} + e_{22}), \\ k_{12} &= k_1 e_{12}, \\ k_{23} &= k_{31} = 0, \end{aligned} \tag{3·2}$$

so that relations (2·3) reduce to

$$\begin{aligned} D_1 &= [k + (k_1 + k_2) e_{11} + k_2 e_{22}] E_1 + k_1 e_{12} E_2, \\ D_2 &= [k + (k_1 + k_2) e_{22} + k_2 e_{11}] E_2 + k_1 e_{12} E_1, \\ D_3 &= [k + k_2 (e_{11} + e_{22})] E_3. \end{aligned} \tag{3·3}$$

Equations (2·7) is satisfied if

$$E_1 = -\frac{\partial v}{\partial x}, E_2 = -\frac{\partial v}{\partial y}, E_3 = 0, \tag{3·4}$$

where the electric polential $v(x, y)$ is a function of x and y only.

In the absence of P_1, the equation (2·8) combined with the relations (3·3) gives

$$\begin{aligned}
&[k + (k_1 + k_2)\, e_{11} + k_2\, e_{22}]\frac{\partial^2 v}{\partial x^2} \\
&+ [k + (k_1 + k_2)\, e_{22} + k_2\, e_{11}]\ \frac{\partial^2 v}{\partial y^2} + 2k_1\, e_{12}\frac{\partial^2 v}{\partial x \partial y} \\
&+ \left[(k_1 + \quad)\ \frac{\partial e_{11}}{\partial x} + k_2\ \frac{\partial e_{22}}{\partial y} + k_1\ \frac{\partial e_{12}}{\partial y} \right] \frac{\partial v}{\partial x} \\
&+ \left[(k_1 + k_2)\ \frac{\partial e_{22}}{\partial y} + k_2\ \frac{\partial e_{11}}{\partial y} + k_1\ \frac{\partial e_{12}}{\partial x} \right] \frac{\partial v}{\partial y} = 0.
\end{aligned} \tag{3·5}$$

Moreover, relations (2·1) simplify to

$$\begin{aligned}
\sigma_{11} &= (\lambda + 2\mu)\, e_{11} + \lambda e_{22} + (a + b)\, E_1^2 + bE_2^2, \\
\sigma_{22} &= (\lambda + 2\mu)\, e_{22} + \lambda e_{11} + (a + b)\, E_2^2 + bE_1^2 \\
\sigma_{33} &= \lambda\, (e_{11} + e_2\ ) + b\, (E_1^2 + E_2^2) \\
\sigma_{12} &= 2\mu\, e_{12} + a.\, E_1 E_2, \\
\sigma_{23} &= \sigma_{31} = 0.
\end{aligned} \tag{3·6}$$

From the first two relations above it is easily found that

$$\begin{aligned}
e_{11} = \frac{1}{4\mu\,(\lambda + \mu)} &[\,(\lambda + 2\mu)\,\{\sigma_{11} - (a + b)\, E_1^2 - b\, E_2^2\} \\
&- \lambda\,\{\sigma_{22} - (a + b)\, E_2^2 - b\, E_1^2\},
\end{aligned}$$

$$\begin{aligned}
e_{22} = \frac{1}{4\mu\,(\lambda + \mu)} &[\,(\lambda + 2\mu)\,\{\sigma_{22} - (a + b)\, E_2^2 - b\, E_1^2\} \\
&- \lambda\,\{\sigma_{11} - (a + b)\, E_1^2 - b\, E_2^2\}\,]
\end{aligned} \tag{3·6a}$$

While we may write the fourth relation as

$$e_{12} = \frac{1}{2\mu}\,(\sigma_{12} - a\, E_1 E_2) \tag{3·6b}$$

In problems of plane strain, equations (2·6) imply

$$\frac{\partial \sigma_{11}}{\partial x} + \frac{\partial \sigma_{12}}{\partial y} = 0, \qquad \frac{\partial \sigma_{12}}{\partial x} + \frac{\partial \sigma_{22}}{\partial y} = 0.$$

These are satisfied if

$$\sigma_{11} = \frac{\partial^2 \varphi}{\partial y^2}, \sigma_{22} = \frac{\partial^2 \varphi}{\partial x^2}, \sigma_{12} = -\frac{\partial^2 \varphi}{\partial x \partial y} \tag{3·7}$$

where φ is the stress function.

The compatibility relation between the strain components is

$$2\frac{\partial^2 e_{12}}{\partial x \partial y} = \frac{\partial^2 e_{11}}{\partial y^2} + \frac{\partial^2 e_{22}}{\partial x^2}.$$

Substituting in it the values of e_{11}, e_{22} and e_{12} as obtained from (3·6*a*) and (3·6*b*) and then introducing the stress function φ and electrical potential v with the help of (3·4) and (3·7) we obtain

$$\nabla^4\varphi + \frac{4(\lambda+\mu)\,a}{\lambda+2\mu}\frac{\partial^2}{\partial x\partial y}\left(\frac{\partial v}{\partial x}\cdot\frac{\partial v}{\partial y}\right) - \left[\left(\frac{\partial^2}{\partial y^2} - \frac{\lambda}{\lambda+2\mu}\frac{\partial^2}{\partial x^2}\right)\left\{(a+b)\left(\frac{\partial v}{\partial x}\right)^2 + b\left(\frac{\partial v}{\partial y}\right)^2\right\} + \left(\frac{\partial^2}{\partial x^2} - \frac{\lambda}{\lambda+2\mu}\frac{\partial^2}{\partial y^2}\right)\left\{(a+b)\left(\frac{\partial v}{\partial y}\right)^2 + b\left(\frac{\partial v}{\partial x}\right)^2\right\}\right] = 0 \tag{3·8}$$

Again, eliminating the strain components in (3·5) with the help of (3·6*a*) and (3·6*b*), and introducing by (3·7) we get, after some lengthy calculations, the operational equation

$$k\nabla^2 v + \frac{1}{4\mu(\lambda+\mu)}\left[\left\{(\lambda k_1 - 2\mu b)\left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial v}{\partial x}\cdot\frac{\partial}{\partial x}\right) - (\lambda k_1 - 2\mu k_2)\left(\frac{\partial^2 v}{\partial y^2} + \frac{\partial}{\partial y}\cdot\frac{\partial}{\partial y}\right)\right\}\left\{\frac{\partial^2\varphi}{\partial y^2} - (a+b)\left(\frac{\partial v}{\partial x}\right)^2 - b\left(\frac{\partial v}{\partial y}\right)^2\right\} + \left\{(\lambda k_1 - 2\mu b)\left(\frac{\partial^2 v}{\partial y^2} + \frac{\partial v}{\partial y}\cdot\frac{\partial}{\partial y}\right) - (\lambda k_1 - 2\mu k_2)\left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial v}{\partial x}\cdot\frac{\partial}{\partial x}\right)\right\}\left\{\frac{\partial^2\varphi}{\partial x^2} - (a+b)\left(\frac{\partial v}{\partial y}\right)^2 - b\left(\frac{\partial v}{\partial x}\right)^2\right\}\right] - \frac{k_1}{2\mu}\left[\left(2\frac{\partial^2 v}{\partial x\partial y} + \frac{\partial v}{\partial x}\cdot\frac{\partial}{\partial y} + \frac{\partial v}{\partial y}\cdot\frac{\partial}{\partial x}\right)\left(\frac{\partial^2\varphi}{\partial x\partial y} + a\frac{\partial v}{\partial x}\cdot\frac{\partial v}{\partial y}\right)\right] = 0. \tag{3·9}$$

The simultaneous equations (3·8) and (3·9) determine the function φ and v, when appropriate conditions are prescribed. These equations are highly non-linear and are coupled with each other in the complicated way.

To the first approximation, it may be assumed that the medium does not become electrically anisotropic, that is, we may set

$$k_1 = k_2 = 0, \tag{3·10}$$

so that the equation (3·9) simplified to

$$\nabla^2 v = 0, \tag{3·11}$$

while equation (3·8) becomes

$$\nabla^4\varphi + \frac{8(\lambda+\mu)k}{\lambda+2\mu}\frac{\partial^2}{\partial x\partial y}\left(\frac{\partial v}{\partial x}\,\frac{\partial v}{\partial y}\right) - 2k\left[\left(\frac{\partial^2}{\partial y^2} - \frac{\lambda}{\lambda+2\mu}\frac{\partial^2}{\partial x^2}\right)\left\{\left(\frac{\partial v}{\partial x}\right)^2\right\} + \left(\frac{\partial^2}{\partial y^2} - \frac{\lambda}{\lambda+2\mu}\frac{\partial}{\partial y^2}\right)\left\{\left(\frac{\partial v}{\partial y}\right)^2\right\}\right] = 0. \tag{3·12}$$

Equation (3·11) may be solved for v as in classical problems. Substitution of this value of v in (3·12) yields a linear equation in φ. The solution obtained in this way may be called the uncoupled solution.

The uncoupled solution may be used as the starting solution for the application of the method of perturbation, if the electrically property of the medium becomes only slightly anisotropic after the deformation.

The theory outlined above will be illustrated in subsequent sections by solving a special problem.

4. Bending of a clamped plate

We consider the bending of a long strip plate of thickness clamped at one end, the opposite edge being subjected to mechanical forced. (Fig. 1). The solution of the problem when the electrical forced are absent in well-known [5].

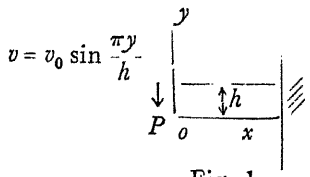


Fig. 1

We take the axis of z along the length of the plate, and the axes of x and y along its breadth and thickn ss respectively. For the plane strain problem. We need consider only a cross section of the plate, which is taken to be the xy – plane.

The mechanical boundary conditions are that the edges $y = 0$ and $y = h$ of the cross section are free from the mechanical stresses and the edge has a distribution of shear forced equivalent to a load P.

As per the electrical boundary conditions we assume that the edge $x = 0$ has the prescribed potential

$$v(o, y) = v_0 \sin \frac{\pi y}{h} \tag{4·1}$$

and the edges $y = 0$ and $y = h$ are at zero potentials. We also assume that the breadth of the plate is sufficiently large in comparison with its thickness so that the clamped edge may be considered to be at zero potential.

We shall first show that these boundary conditions are compatible for maintaining equilibrium of the plate if the electric property remains isotropic after d formation. In other words, the uncoupled solution will be obtained corresponding to these boundary conditions. We shall then obtain a coupled solution by the perturbation method and examine how far these boundary conditions may be maintained when the medium becomes asisotropic due to deformation.

4'(a). Uncoupled solution

In this section we obtain the uncoupled solution. The solution of equation (3·11) for the function consistent with the boundary condition (4·1) and other stated thereafter are

$$v(x, y) = v_0 e^{-\frac{\pi x}{h}} \sin \frac{\pi y}{h} \tag{4·2}$$

substituting this value of v in (3·12) we obtain

$$\nabla^4 p = \frac{\alpha^4 v_0^{\,2} k}{2(\lambda + 2\mu)} e^{-\alpha x} [\mu + 4(\lambda + \mu) \cos \alpha y], \tag{4·3}$$

where $$\alpha = \frac{2\pi}{h} \tag{4·4}$$

The solution of the equation (4·3) may be taken as

$$\varphi = -\frac{P}{h^3} xy^2 (3h - 2y)$$
$$+ e^{-\alpha x} (c_1 \cos \alpha y + c_2 \sin \alpha y + c_3 y \cos \alpha y + c_4 y \sin \alpha y)$$
$$+ e^{-\alpha x} (c_5 - c_6 \alpha^2 y^2 \cos \alpha y), \tag{4·5}$$

where $$c_5 = \frac{\mu v_0^2 k}{2(\lambda + 2\mu)}, \; c_6 = \frac{(\lambda + \mu) v_0^2 k}{4(\lambda + 2\mu)}. \tag{4·6}$$

The coefficients c_1, c_2, c_3 and c_4 are to be determined from the mechanical boundary conditions, and P represents the total mechanical load applied at the edge $x = 0$. The first term in the right hand side of (4·5) is the classical solution of the problem when the effect of the electric field is not considered, the second term is the complimentary function for the differential equation and the third term is the particular integral.

Now, the conditions

$$\sigma_{22} = \frac{\partial^2 \varphi}{\partial x^2} = 0 \qquad \text{at} \qquad y = 0, \text{ and } y = h.$$

When applied to (4·5), give

$$c_1 = -c_5, \quad c_3 = \alpha^2 h c_6. \tag{4·7}$$

Similarly the conditions

$$\sigma_{12} = -\frac{\partial^2 \varphi}{\partial x \partial y} = 0, \text{ at } y = 0, \text{ and } y = h$$

implies

$$c_2 = -\alpha h c_6, \quad c_4 = 2\alpha c_6 \tag{4·8}$$

It may be easily verified that

$$\int_0^h (\sigma_{12})_{x=0} \, dy = P, \tag{4·9}$$

$$\int_0^h (\sigma_{11})_{x=0} \, dy = 0 \tag{4·10}$$

which are the required mechanical conditions on the surface $x = 0$.

Substituting the values of the constants from (4·7) and (4·8) in (4·5) we obtain the stress function

$$\varphi = -\frac{P}{h^3} xy^2 (3h - 2y) + e^{\alpha x} [c_5 - (c_5 - c_6 \alpha^2 hy + c_6 \alpha^2 y^2)$$
$$\cos \alpha y - c_6 \alpha (h - 2y) \sin \alpha y]. \tag{4·11}$$

The corresponding stresses are obtained as follows:

$$\sigma_{11} = -\frac{6P}{h^3} x (2h - 2y) + \alpha^2 e^{-\alpha x} [(c_5 + 2c_6 - c_6 \alpha^2 hy$$
$$+ c_6 \alpha^2 y^2) \cos \alpha y - c_6 \alpha (h - 2y) \sin \alpha y], \tag{4·12}$$

$$\sigma_{22} = \alpha^2 e^{-\alpha x} [c_5 - (c_5 - c_6 \alpha^2 hy + c_6 \alpha^2 y^2) \cos \alpha y - c_6 \alpha (h - 2y) \sin \alpha y], \tag{4·13}$$

$$\sigma_{12} = \frac{6P}{h^3} y (h - y) + \alpha^2 e^{-\alpha x} (c_5 + 2c_6 - c_6 \alpha^2 hy + c_6 \alpha^2 y^2) \sin \alpha y. \tag{4·14}$$

For later reference we shall require the following result :

$$\sigma_{11} + \sigma_{22} = \nabla^2\varphi$$

$$= -\frac{6P}{h^3}\, x\,(h-2y) + \alpha^2\, e^{-\alpha x}\,[c_5 + 2c_6 \cos \alpha y - 2\, c_6\, \alpha\,(h-2y) \sin \alpha y] \qquad (4\cdot15)$$

4(*b*) Coupled Solution

Since there are two material parameters k_1 and k_2 which introduce electrical anisotropy, we may assume one of them to be zero for the purpose of studying the effect of the other. In fact the electrostrictive effect of the shear strain is much smaller than that of the dilatation [3], so that k_2 is much larger than k_1 in the relation (2·4). Hence we may assume

$$k_1 = 0, \quad k_2 \neq 0. \qquad (4\cdot16)$$

Then equations (3·8) and (3·9) simplify to

$$\nabla^4\varphi + \frac{8\,(\lambda+\mu)\,k}{\lambda+2\mu}\,\frac{\partial^2}{\partial x \partial y}\left(\frac{\partial v}{\partial x}\cdot\frac{\partial v}{\partial y}\right) - \left[\left(\frac{\partial^2}{\partial y^2} - \frac{\lambda}{\lambda+2\mu}\,\frac{\partial^2}{\partial x^2}\right)\left\{(2k-k_2)\left(\frac{\partial v}{\partial x}\right)^2 - k_2\left(\frac{\partial v}{\partial y}\right)^2\right\} + \left(\frac{\partial^2}{\partial x^2} - \frac{\lambda}{\lambda+2\mu}\,\frac{\partial^2}{\partial y^2}\right)\left\{(2k-k_2)\left(\frac{\partial v}{\partial y}\right)^2 - k_2\left(\frac{\partial v}{\partial x}\right)^2\right\}\right] = 0. \qquad (4\cdot17)$$

$$\nabla^2 v + \frac{k_2}{2k\,(\lambda+\mu)}\left[\left(\nabla^2 v + \frac{\partial v}{\partial x}\cdot\frac{\partial}{\partial x} + \frac{\partial v}{\partial y}\cdot\frac{\partial}{\partial y}\right)\left\{\nabla^2\varphi - 2(k-k_2)\left[\left(\frac{\partial v}{\partial x}\right)^2 + \left(\frac{\partial v}{\partial y}\right)^2\right]\right\}\right] = 0. \qquad (4\cdot18)$$

If the anisotropic effect is small, *i.e.*, k_2 is small, we take

$$\varphi = F_0 + k_2 F_1 + k_2^2 F_2 + \ldots ; \; v = f_0 + k_2 f_1 + k_2^2 f_2 + \qquad (4\cdot19)$$

so that the functions F_0 and f_0 correspond to the uncoupled solution as obtained in the previous sub-section.

Now, substituting the value of φ and v from (4·19) in (4·17) and (4·18), and equating the coefficient of k_2 to zero, we obtain

$$\nabla^4 F_1 + \frac{8\,(\lambda+\mu)k}{\lambda+2\,\mu}\,\frac{\partial^2}{\partial x \partial y}\left(\frac{\partial f_0}{\partial x}\,\frac{\partial f_1}{\partial y} + \frac{\partial f_1}{\partial x}\cdot\frac{\partial f_0}{\partial y}\right) - \left[\left(\frac{\partial^2}{\partial y^2} - \frac{\lambda}{\lambda+2\mu}\,\frac{\partial^2}{\partial x^2}\right)\left\{4k\,\frac{\partial f_0}{\partial x}\cdot\frac{\partial f_1}{\partial x} - \left(\frac{\partial f_0}{\partial x}\right)^2 - \left(\frac{\partial f_0}{\partial y}\right)^2\right\} + \left(\frac{\partial^2}{\partial x^2} - \frac{\lambda}{\lambda+2\mu}\,\frac{\partial^2}{\partial y^2}\right)\left\{4k\frac{\partial f_0}{\partial y}\cdot\frac{\partial f_1}{\partial y} - \left(\frac{\partial f_0}{\partial x}\right)^2 - \left(\frac{\partial f_0}{\partial y}\right)^2\right\}\right] = 0 \qquad (4\cdot20)$$

$$\nabla^2 f_1 + \frac{k_2}{2k\,(\lambda+\mu)}\left[\left(\nabla^2 f_0 + \frac{\partial f_0}{\partial x}\cdot\frac{\partial}{\partial x} + \frac{\partial f_0}{\partial y}\cdot\frac{\partial}{\partial y}\right)\left\{\nabla^2 F_0 - 2k\left[\left(\frac{\partial f_0}{\partial x}\right)^2 + \left(\frac{\partial f_0}{\partial y}\right)^2\right]\right\}\right] = 0 \qquad (4\cdot21)$$

The values of f_0 and F_0 are those of v and φ as given in (4·2) and (4·11) resepctively. Substitution of these values in (4·12) we have

$$\nabla^2 f_1 = -\beta e^{-\frac{\alpha x}{2}}\left[\frac{6P}{h^3}(h-2y)\sin\frac{\alpha y}{2} + \frac{12p}{h^3}\, x\cos\frac{\alpha y}{2}\right.$$
$$+ \alpha_3\left(c_5 - c_6 + \frac{v_0{}^2 k}{2}\right)e^{-\alpha x}\sin\frac{\alpha y}{2}$$
$$\left. + c_6\,\alpha^3 e^{-\alpha x}\sin\frac{3\alpha y}{2} - 2c_6\,\alpha^4 e^{-\alpha x}(h-y)\cos\frac{\alpha y}{2}\right],$$

where
$$\beta = \frac{k_2\, v_0 \alpha}{4k\,(\lambda+\mu)} \tag{4·22}$$

The solution of this equation may be written as

$$f_1(x,y) = f_{10}(x,y) + f_{11}(x,y) \tag{4·23}$$

where f_{10} is the complementary functions satisfying the equation

$$\nabla^2 f_{10} = 0 \tag{4·24}$$

and f_{11} is the particular integral having the following value :

$$f_1(x,y) = \beta\left[\frac{6P}{\alpha^3 h^3}\left\{\alpha^2(hy-y^2)\cos\frac{\alpha y}{2} + 2\alpha y\sin\frac{\alpha y}{2} + \alpha x(1+\alpha x)\cos\frac{\alpha y}{2}\right\}e^{-\frac{\alpha x}{2}}\right.$$
$$- \frac{\alpha}{2}\left(c_5 - c_6 + \frac{v_0{}^2 k}{2}\right)e^{-\frac{3\alpha x}{2}}\sin\frac{\alpha y}{2} + \tfrac{1}{3}\,c_6\,\alpha^2 x\, e^{-\frac{3\alpha x}{2}}\sin\frac{3\alpha y}{2}$$
$$\left. + c_6\alpha\, e^{-\frac{3\alpha x}{2}}\left\{\alpha(h-y)\cos\frac{\alpha y}{2} - \sin\frac{\alpha y}{2}\right\}\right] \tag{4·25}$$

The boundary conditions on $f_1(x,y)$ are that

$$f_1(0,y) = f_1(x,0) = f_1(x,h) = 0 \tag{4·6a}$$

and also $f_1(x,y)$ tends to zero as x tends to large values. These are satisfied by taking

$$f_{10}(0,y) = -\beta\left[\frac{6P}{\alpha^3 h^3}\left\{\alpha^2(hy-y^2)\cos\frac{\alpha y}{2} + 2\alpha y\sin\frac{\alpha y}{2}\right\} - \frac{\alpha}{2}\left(c_5 - c_6 + \frac{v_0{}^2 k}{2}\right)\sin\frac{\alpha y}{2}\right.$$
$$\left. + c_6\,\alpha\left\{\alpha(h-y)\cos\frac{\alpha y}{2} - \sin\frac{\alpha y}{2}\right\}\right], \tag{4·27}$$

$$f_{10}(x,0) = \beta\left[\frac{6P}{\alpha^3 h^3}\,\alpha x(1+\alpha x)\,e^{-\frac{\alpha x}{2}} + c_6\,\alpha^2 h\, e^{-\frac{3}{2}\alpha x}\right] \tag{4·28}$$

$$f_{10}(x,h) = -\frac{6P}{\alpha^3 h^3}\,\beta\,\alpha x(1+\alpha x)e^{-\frac{\alpha x}{2}} \tag{4·29}$$

To satisfy equations (4·24) and conditions from (4·27) to (4·29), let us assume

$$f_{10}(x,y) = f_{12}(x,y) + \beta\left[\frac{\alpha}{2}\left(c_5 + c_6 + \tfrac{1}{2}v_0{}^2 k\right)e^{-\frac{\alpha x}{2}}\sin\frac{\alpha y}{2}\right.$$
$$\left. + \sum_{n=0}^{\infty} A_n\, e^{-\frac{n\pi x}{2}}\cos\frac{n\pi y}{h} + \sum_{n=1}^{\infty} B_n\, e^{-\frac{n\pi x}{h}}\sin\frac{n\pi y}{h}\right], \tag{4·30}$$

where $f_{12}(x,y)$ is the solution of the equation

$$\nabla^2 f_{12} = 0 \tag{4·31}$$

and the coefficients A_n and B_n are to be so chosen that the condition (4·27) is satisfied. That is, we take

$$c_6\alpha^2\,(h-y)\cos\frac{\alpha y}{2} = \sum_{n=0}^{\infty} A_n \cos\frac{n\pi y}{h},$$

$$-\frac{6p}{\alpha^3h^3}\left\{\alpha^2\,(hy-y^2)\cos\frac{\alpha y}{2} + 2\,\alpha y\sin\frac{\alpha y}{2}\right\} = \sum_{n=1}^{\infty} B_n \sin\frac{n\pi y}{h}. \quad (4\cdot32)$$

By Fourier sine and cosine series, the coefficients A_n and B_n are evaluated as follows :

$$A_1 = \tfrac{1}{2}\,c_6\,\alpha^2 h,$$

$$A_n = \frac{2}{\pi}c_6\,\alpha^2 h\frac{n^2+1}{(n^2-1)^2}\{1+(-1)^n\},\ \text{if } n \neq 1, \quad (4\cdot33)$$

$$B_1 = -\frac{6P}{\alpha^2h^2},$$

$$B_n = -\frac{12P}{\pi^2\alpha^2h^2}\left\{\frac{\alpha h}{\pi}\cdot\frac{2n\,(n^3+3)}{(n^2-1)^3} - \frac{4n}{(n^2-1)^2}\right\}\{1+(-1)^n\},\ \text{if } n\neq 1, \quad (4\cdot34)$$

From (4·27), (4·28) and (4·30), it is seen that the boundary conditions on $f_{12}(x, y)$ are

$$f_1(0, y) = 0 \quad (4\cdot35)$$

$$f_{12}(x, 0) = \beta\left[\frac{6P}{\alpha^3h^3}\cdot\alpha x\,(1+\alpha x)\,e^{-\frac{\alpha x}{2}} + c_6\,\alpha^2 h\;e^{-\frac{3}{2}\alpha x} - \sum_{n=0}^{\infty}A_n\,e^{-\frac{n\pi x}{h}}\right], \quad (4\cdot36)$$

$$f_{12}(x, h) = -\beta\left[\frac{6P}{\alpha^3h^3}\cdot\alpha x\,(1+\alpha x)e^{-\frac{\alpha x}{2}} - \sum_{n=0}^{\infty}(-1)^n A_n\,e^{-\frac{n\pi x}{h}}\right], \quad (4\cdot37)$$

It follows from (4·33) that

$$A_n = (-1)^n A_n,\ \text{if } n \neq 1.$$

Let the solution of (4·31) be taken as

$$f_{12}(x, y) = \int_0^{\infty}\{F(\xi)\;e^{\xi y} + G(\xi)\;e^{-\xi y}\}\sin(\xi x)\,d\xi, \quad (4\cdot38)$$

so that the conditions (4·35) is satisfied, and we have

$$f_{12}(x, 0) = \int_0^{\infty}\{F(\xi) + G(\xi)\}\sin(\xi x)\,d\xi, \quad (4\cdot39)$$

$$f_{12}(x, h) = \int_0^{\infty}\left\{F(\xi)\,e^{\xi h} + G(\xi)\,e^{-\xi h}\right\}\sin(\xi x)\,d\xi$$

From these relations, we obtain by Fourier sine transforms,

$$F(\xi) + G(\xi) = \frac{2}{\pi}\int_0^{\infty} f_{12}(x, 0)\sin(\xi x)\,dx,$$

$$F(\xi)\,e^{\xi h} + G(\xi)\,e^{-\xi h} = \frac{2}{\pi}\int_0^{\infty} f_{12}(x, h)\sin(\xi x)\,dx \quad (4\cdot40)$$

Substituting the values of $f_{12}(x, 0)$ and $f_{12}(x, h)$ from (4·36) and (4·37) and denoting the integrated results by I_1 and I_2 we obtain the following results on simplification.

$$F(\xi) = \frac{I_2 - I_1\,e^{-\xi h}}{2\sinh(\xi h)}$$

$$G(\xi) = \frac{I_1\,e^{\xi h} - I_2}{2\sinh(\xi h)} \quad (4\cdot41)$$

where

$$I_1 = \frac{2\beta}{\pi}\left[\frac{6P}{ah^3}\cdot\frac{\xi\left(\frac{7\pi^2}{h^2}-\xi^2\right)}{\left(\frac{\pi^2}{h^2}+\xi^2\right)^3}+\frac{c_6 a^3 h^3}{\frac{9\pi^2}{h^2}+\xi^2}-\sum_{n=0}^{\infty}\frac{A_n\,\xi}{\frac{n^2\pi^2}{h^2}+\xi^2}\right]$$

$$I_2 = -\frac{2\beta}{\pi}\left[\frac{6P}{ah^3}\cdot\frac{\xi\left(\frac{7\pi^2}{h^2}-\xi^2\right)}{\left(\frac{\pi^2}{h^2}+\xi^2\right)^3}-\sum_{n=0}^{\infty}\frac{(-1)^n A_n\,\xi}{\frac{n^2\pi^2}{h^2}+\xi^2}\right] \qquad (4\cdot42)$$

The values of $F(\xi)$ and $G(\xi)$ are now substituted in (4·38). For conciseness, we introduce the integral

$$S^{m}_{n,r}(y) = \int_0^{\infty}\frac{\xi^m}{\left(\frac{n^2\pi^2}{h^2}+\xi^2\right)^r}\frac{\sinh(\xi y)}{\sinh(\xi h)}\sin(\xi x)\,d\xi \qquad (4\cdot43)$$

where $h > y > 0$, $x > 0$, and m, n, r are positive integers. The value of this integral when $m = r = 0$ are known [6]. For other values of m and r, numerical methods may be adopted for the evaluation of the integral. In terms of these integrals, the expression for $f_{12}(x, y)$ is finally obtained as :

$$f_{12}(x,y) = \frac{2\beta}{\pi}\left[\frac{6p}{ah^3}\left\{\frac{7\pi^2}{h^2}S^1_{1,3}(h-y)-\frac{7\pi^2}{h^2}S^1_{1,3}(y)\right.\right.$$

$$\left.S^3_{1,3}(h-y)+S^3_{1,3}(y)\right\}-\sum_{n=0}^{\infty}A_n\left\{S^1_{n,1}(h-y)+(-1)^{n+1}S^1_{n,1}(y)\right.$$

$$\left.+c_6 a^2 h S^1_{3,1}(h-y)\right] \qquad (4\cdot44)$$

Thus the purturbed potential function is given by (4·23) when (4·25), (4·30) and (4·44) are used. If it is desired to obtain the purturbed stress function F_1, the equation (4·21) may be used. In it the values of $f_0(x, y)$ and $f_1(x, y)$ are to be substituted and the equation may be integrated with proper boundary conditions. Since we have already obtained a modified form of the stress functon in (4·11), we refrain from obtaining its purturbed terms in introduce further modifications.

Lastly, it may be mentioned that the present discussion clearly points out the fact that the solution of special problems of plane strains in electrostriction is very complicated and the subject possesses vast potentiality of researches. Incidentally, we have come across an integral in (4·43) whose analytical evaluation is also a subject of further investigation.

References

1. Landau, L. D. and Lifshitr, E. M., Electrodynamics of Continuous Media Addition—*Wesley*, 1960.
2. Stratton, J. D. Electromagnetic Theory, London, 1941.
3. Krishnan, R. S., Progress in Crystal Physics. Vol. I, New York, 1958.
4. Knops, R. J.
   (*i*) Electrostrictive Deformation of Composite Dielectric, *Brown Unir. Report* 1961.
   (*ii*) A Reciprocal Theorem for a first order theory of Electrostriction.
5. Timoshenko, S. P. and Goodier, J. N., Theory of Elasticity. *Asian Students' Edition*, p. 35.
6. Erdelyi, A., (editor), Tables of Integral Transforms. Vol. I, 1954, p. 88.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968.

Studies on Biogas Production (I)—Methane Fermention of some Carbohydrates

By

C. R. TRASAD,[1] K. C. GULATI, M. A. IDNANI & R. S. DEWAN

Division of Soil Science and Agricultural Chemistry, Indian Agricultural Research Institute, New Delhi-12

[Received on 30th August, 1966]

Methane is a characteristic product of microbial decomposition of organic materials. The evolution of marsh gas from decaying vegetation in swamps and lakes during summar season when microbial activities are high, is a conspicuous phenomenon. The gas consits largely of methane with smaller amount of carbon-di-oxide and sometimes a little hydrogen (Barker, 1956). Mixed species of methane bacterial utilize not only various types of pure organic compounds but also organic materials of plant and animal origin under restricted oxygen supply. Studies by Tarvin *et al.* (1934), indicated that hydrogen to the extent of 30 percent in the gas components was obtained when carbohydrate was used as substrate. Various workers (Buswell *et al.* 1962 ; Rufener *et al.*, 1963 ; Hende *et al.*, 1963) have reported the formation of volatile fatty acids like acetic, propinonic and butyric in the media during decomposition of various organic materials by methane formers.

The present investigations were carried out to make an exploratory study to examine the behaviour of organism, dominated by a mixed species of methane formers, towards the breakdown of carbohydrates such as glucose, sucrose, maltose, cellobiose, lactose, cellulose and starch and complex polysaccharides like, gum arabic and hemicellulose, producing methane. The carbohydrates mentioned above differ in their chain lengths, complexity and linkages. Alongside, the studies were also made to determine the total acidity and the type of volatile fatty acids formed after anaerobic fermentation of these carbohyorates at different concentrations.

Materials and Methods

0·5 g each of oven-dry glucose (BDH), sucrose (AR), maltose (BDH), cellobiose (AR), lactose (pharmaceutical grade), starch (Merck), cellulose (Whatman filter paper No. 1), gum arabic (*Ex Acaceae arabica*) and hemicelluloses (Ex. Aspan) was dissolved/suspended in 100 ml. distilled water. One percent nitrogen in the form of diammonium hydrogen phosphate, calculated on the basis of the weight of the substrate, was added before fermentation in order to supply major nutrients to the organisms. The medium in each case was inoculated with 10 ml. of incoculum finally making a total volume of 200 ml. The incoculum was prepared by filtering the spent slurry (obtained from the cow dung gas plant of the Division of Chemistry, I. A. R. I. New Delhi) through a mat of powdered wheat straw to remove as far as practicable, all solid materials other than bacterial cells. The

1. Part of the investigations carried out (by C. R. Prasad) in partial requirements for the degree of Doctor of Philosophy, P. G. School, Indian Agricultural Research Institute, Delhi.

Present Address : Chittaranjan Prasad, Assistant Agricultural Chemist, Agril. Research Institute, Kanke (P. O.) Ranchi (Bihar).

fermentation was carried out at 30-32°C in an incubator. When about a litre of gas was evolved, it was analysed twice for carbondioxide, oxygen, carbon monoxide, methane, hydrogen, and nitrogen (by difference) prior to adjustment of pH of the media. The analysis was done in a gas analyser of German make, based upon Orsaat's principle (Treadwell and Hall, 1948). At the end of fermentation reaction the pH of the subtrate was adjusted to 7·5 with sodium hydroxide: Reinoculation with 10 ml of inoculum and incubating as before restarted the fermentation reaction. The gas, thus evolved, was again analysed twice as before. In the case of cellulose the fermentation was allowed to proceed continuously and pH adjustment was not necessary. Total acidity and the type of volatile fatty acids produced after anaerobic fermentation of carbohydrates were also determined.

For this pupose fermentation was allowed to proceed using 0·25, 0·50, 0·75, and 1·0 % solution of the carbohydrates (except, cellobiose and hemi-cellulose), pH and total acidity were determined after 10 days when fermentation practically stopped. The total acidity was determined by titrating potentiometrically in 50 ml. of the substrate with 0·1 N sodium hydroxide, to pH 7·0. It was expressed as ml. of decinormal sodium hydroxide required to nutralise acid present in 100 ml. of the substrate. The results are given in Table 3. The nature of volatile fatty acids was measured according to the method of McElvain (1946) in the fermentations carried out with 0·25 and 1·0 % solutions. 100 ml. of the substrate, after the reaction was complete, was distilled and three 10 ml. portions of the distillates were collected consecutively into three graduated cylinders of 10 ml. capacity. Each portion was titrated against 0·1 N sodium hydroxide solution using phenolphthalein as indicator. From the titre values, the Duclaux values were culculated as follows :

$$\text{Duclaux Value} = \frac{\text{ml. of alkali required for first (second or third 10 ml. of distillate)} \times 100}{\text{ml. of alkali required for 100 ml. of the original solution}}$$

The Duclaux values calculated as above are shown in Table 4.

Results and Discussion

The experimental results with respect to average percentage composition (average of two determinations) of the various components of gas samples collected twice before adjustment of pH of media and the same number of times after adjustment of pH are given in Tables 1 and 2 respectively.

TABLE 1

Analyses of gas samples from different carbohydrates (before pH adjustment)

No.	Compounds	Percentage composition of gas			
		CO_2	CH_4	H_2	N_2
1.	Glucose	49·6	0·8	49·3	0·3
2.	Sucrose	50·0	1·0	47·9	1·1
3.	Maltose	49·6	0·8	49·3	0·3
4.	Cellobiose	50·0	1·0	47 9	1·1
5.	Lactose	50·0	1·0	47·9	1·1
6.	Starch	51·2	12·8	35·7	0·3
7.	Gum arabic	50·4	38·4	11·2	0·0
8.	Hemicellulose	50·2	42·8	6·8	0 2
9.	Cellulose (Filter paper)	48·8	48·30	3·2	0·0

TABLE 2

Analyses of gas samples from different carbohydrates (after pH adjustment)

No.	Compounds	Percentage composition of gas			
		CO_2	CH_4	H_2	N_2
1.	Glucose	20·0	80·0	0·0	0·0
2.	Sucrose	20·8	79·2	0·0	0·0
3.	Maltose	20·8	79·2	0·0	0·0
4.	Cellobiose	20·4	79·6	0·0	0·0
5.	Lactose	20·0	80·0	0·0	0·0
6.	Starch	20·0	76·4	3·2	0·4
7.	Gum arabic	20·4	76·8	2·2	0·6
8.	Hemicellulose	20·5	77·8	1·7	0·0
9.	Cellulose (Filter paper)	48·8	48·0	3·2	0·0

The results given in Tables 1 and 2 indicate that the fermentation reaction proceeded in at least two steps—a brisk evolution of gas mixture of low methane content with the development of acidity and slowing down of the reaction. This is followed by renewed evolution of gas mixture of high methane content after adjustment of pH of the media to 7·5. The methane was as high as to about 80 percent. In case of cellulose however, the fermentation reaction was a continuous one and the percentages of methane, carbondioxide and hydrogen remained nearly constant throughout. The results also show that the proportion of methane obtained in anaerobic ferementation of the above materials increased with the molecular size and complexity of the carbohydrates. The hydrogen content followed the reverse trend Oxygen and carbon monoxide were absent. The composition of gas obtained from the first stage decomposition of glucose and the mono-saccharide and disaccharides used was almost the same, hydrogen and carbon dioxide being the two major components in nearly equal proportions. The more complex carbohydrates produced methane at the expense of hydrogen. A high content of hydrogen (about 30 %) was also found by Tarvin *et al.* (1934) during methane fermentation of carbohydrates. It appears that the mixed and unpurified anaerobic organisms in the crude inoculum used find the complex polysaccharides more favourable for methane fermentation showing that the methane formers are able to thrive better in these media. On the other hand, the simple carbohydrates are more favourable for production of hydrogen and acid.

From Table 3 it is clear that total acid production is much higher in case of mono and disaccharides than in case of cellulose and starch. The total acidity increases, as expected, with the concentration of carbohydrates. The rate of increase is, however, different in different carbohydrates.

In general, fermentation of volatile fatty acids may be regarded as an outcome of any fermentation reaction of organic compounds specially of carbohydrates. The Duclaux values given in Table 4 when compared with those of known fatty acids (McElvain, 1946) indicate that acetic and propionic acid are mainly formed in the fermentation reactions studied here. Buswell *et al.* (1962) also separated and indentified acetic, propionic and butyric acids from anaerobic didestion of sludge.

TABLE 3

pH before and after fermentation of different carbohydrates and total acidity.

No.	Compounds	Substrate concentration (percent)	pH before fermentation	pH after fermentation	Total acidity (ml)
1.	Glucose	0·25	7·6	5·3	12·0
		0·50	7·6	5·1	21·6
		0·75	7·6	4·4	39·4
		1·00	7·6	4·2	46·5
2.	Sucrose	0·25	7·6	5·3	12·4
		0·50	7·6	5·0	21·4
		0·75	7·6	4·5	39·2
		1·00	7·6	4·2	47·0
3.	Maltose	0·25	7·6	5·3	11·8
		0·50	7·6	5·0	21·4
		0·75	7·6	4·8	39·4
		1·00	7·6	3·2	46·8
4.	Lactose	0·25	7·6	5·5	13·0
		0·50	7·6	4·9	52·6
		0·75	7·6	4·5	54·0
		1·00	7·6	4·5	62·0
5	Starch	0·25	7·6	6·4	5·4
		0·50	7·6	6·0	9·6
		0·75	7·6	5·8	12·0
		1·00	7·6	5·6	16·6
6.	Gum arabic	0·25	7·6	6·3	4·0
		0·50	7·6	5·2	21·6
		0·75	7·6	4·8	28·6
		1·00	7·6	4·8	38·4
7.	Cellulose (Filter paper)	0·25	7·6	6·4	5·6
		0·50	7·6	6·2	6·4
		0·75	7·6	6·2	6·8
		1·00	7·6	6·2	7·0

TABLE 4

Nature of volatile fatty acids formed on fermentation of different carbohydrates

No.	Compounds fermented	Concentration (percent)	Corresponding Duclaux values		
			1st Distillate	2nd Distillate	3rd Distillate
1.	Glucose	0·25	10·8	9·6	9·1
		1·00	10·7	9·7	9·0
2.	Sucrose	0·25	9·6	9·4	8·5
		1·00	9·6	9·4	8·5
3.	Maltose	0·25	9·8	8·4	7·0
		1·00	9·7	8·3	7·1
4.	Lactose	0·25	9·7	9·3	8·6
		1·00	9·7	9·3	8·6
5.	Starch	0·25	9·3	7·4	5·5
		1·00	9·3	7·4	5·4
6.	Gum arabic	0·25	7·0	6·5	6·0
		1·00	7·0	6·5	6·0
7.	Cellulose (Filter paper)	0·25	9·4	7·8	7·0
		1·00	9·4	7·8	7·0

Summary

1. Fermentation of carbohydrates like glucose, sucrose, maltose, cellobiose, lactose, starch, gum arabic and hemicellulose by means of inoculum obtained from spent cowdung slurry, showed that the reaction proceeded in atleast two steps, evolution of gas of low methane content with the development of acidity and slowing down of the reaction followed by renewed evolution of gas of high methane content after adjustment of pH of the media to 7 5. In the case of cellulose, however, the fermentation was a continuous one.

2. Analyses of gas samples produced from the above carbohydrates tend to show that prior to adjustment of pH of the media, the proportion of methane in the gas increased with the complexity and the size of the molecules. Glucose and the disaccharides used gave nearly the same composition of gas, high in hydrogen (50%) and low in mathane (1%).

3. The total acidity produced in the media after fermentation was found to be much smaller in the case of the complex carbohydrates than in the case of the simple ones.

4. The calculated Declaux values suggest the presence of acetic and propionic acids particularly the former.

Acknowledgements

The authors acknowledge the keen interest shown by Dr. N. P. Datta, Head of the Division of Soil Science and Agricultural Chemistry, and Dr. K. V. S. Satynarayana, Dr. O. P. Gautam, Dr. W. V. B. Sundara Rao all of the I. A. R. I., Delhi.

References

1. Barker, H. A. Biological formation of methane. *Ind. Eng. Chem.* **48** : 1438-42, 1956.
2. Buswell, A. M., John, R. B. and James, R. M. Paper chromatography for volatile acid determinations. I. A paper chromatographic method for volatile acids. *Eng. Progr. Univ. Florida Tech. Paper*, **16** (9) : 1-7, 1962.
3. Hende, C. V. D., Oyaert, W. and Bouckaert, J. H. Fermentation of serine and threonine by rumen bacteria. *Res. Vet. Sci.*, **4** : 89-95, 1963.
4. McElvain, S. M. The characterization of organic compounds. *The MacMillan Company, New York*, 1946.
5. Rufener, Jr. W. H., Nelson, W. O. and Wolin, M. J. Maintenance of rumen microbial population in continuous culture. *Appl. Microbiol*, **11** : 196-201, 1963.
6. Tarvin, D. and Buswell, A. M. The methane fermentation of organic acids and carbohydrates. *J. Amer. Chem. Soc.*, **56** : 1751-55, 1934.
7. Treadwell, F. P. and Hall, W. T. Analytical Chemistry. **Vol. II**, *John Wiley and Sons, Inc., New York*, 1948.

Proc. Nat. Acad. Sci., India, 38(A), I & II,, 1968

Application of Goodstein's Solution in solving some Diophantine Equations

By

D. RAMESWAR RAO

Research Scholar, Department of Mathematics, Osmania University, Hyderabad-7

[Received on 9th January, 1967]

Abstract

1. The solution of the equation

$$q(p^2 - q^2) = Q(p^2 - Q^2) \qquad (A)$$

was given by R. L. Goodstein[1] as

$$p = h^2 + hk + k^2,\ q = h^2 - k^2,\ Q = 2hk + k^2 \qquad (B)$$

2. I have used the above solution for finding out two-parameter solutions of all the following Diophantine equations.

(The representation $x, y, z \overset{n}{=} X, Y, Z\ (n = 1, 3)$ means that the equations $x + y + z = X + Y + Z$, $x^3 + y^3 + z^3 = X^3 + Y^3 + Z^3$ hold good simultaneously)

2·1 $$x, y, z \overset{n}{=} X, Y, Z,\ (n = 1, 3)$$

2·2 $$x^3 + y^3 + z^3 + u^3 + v^3 = X^3 + Y^3 + Z^3 + U^3 + V^3.$$

2·3 $$x, y, z \overset{n}{=} X, Y, Z\ (n = 2, 4)$$

$$xy, yz, zx \overset{n}{=} XY, YZ, ZX\ (n = 2)$$

2·4 $$x_i, y_i, z_i, u^2, v^2, w^2 \overset{n}{=} X_i, Y_i, Z_i, U^2, V^2, W^2\ (i = 1, 2\ n = 1, 2, 3)$$

2·5 $$x, y, x + y \overset{n}{=} x^{2t}, z^{2t}\ (n = 2, 4)\quad t \geqq 1.$$

2·6 $$x^3 + y^6 + y^6 = X^3 + Y^6 + Y^6$$

2·7 $$x^3 - y^3 = X^2 - Y^2$$

2·8 $$\sum_{i=1}^{3} (x_i^2 - y_i^2) = (x_1^2 + x_2^2) - (y_1^2 + y_2^2 = \sum_{i=1}^{3} (X_i^4 - Y_i^4)$$

2·9 $$x^2 (X^6 - Y^6 - Z^6) = X^2 (x^6 - y^6 - z^6)$$

2·91 $$\frac{x^2 - y^2}{X^2 - Y^2} = z^{2^n}$$

Solutions

3. Solutions of the equations 2·2, 2·3, 2·4 of 2 above are worked out in detail below. Solutions to the others are enumerated. Throughout the treatise the variables p, q, Q have the values ascribed to them in (B).

Equation No. $2\cdot2$:

3·1
$$x = (p^2 - q^2)\,ps,\ y = (2pq + q^2)\,qs,\ z = (2pQ + Q^2)\,pr$$
$$u = (p^2 - Q^2)\,rQ,\ v = rsq\ ;$$
$$X = (p^2 - Q^2)\,pr,\ Y = (2pQ + Q^2)\,Qr,\ Z = (2pq + q^2)\,ps\ ;$$
$$U = (p^2 - q^2)\,qs,\ V = rsQ$$

is a two-parameter solution of

$$x^3 + y^3 + z^3 + u^3 + v^3 = X^3 + Y^3 + Z^3 + U^3 + V^3$$

for if $a = p^2 - q^2,\ b = 2pq + q^2,$

then $$(a^2 + ab + b^2)\,(p^2 + pq + q^2) = (p^2 + pq + q^2)^3.$$

Therefore

$$\frac{(ap)^3 + (bq)^3 - (bp)^3 - (aq)^3}{(p^2 + pq + q^2)^3} - p^3 + q^3 = -3q(p^2 - q^2) = -3Q(p^2 - Q^2)$$

where $p,\ q,\ Q$ are given by (B)

Hence,

$$\frac{\{(p^2 - q^2)p\}^3 + \{(2pq + q^2)q\}^3 - \{(2pq + q^2)p\}^3 - \{(p^2 - q^2)q\}^3}{(p^2 + pq + q^2)^3} + q^3$$
$$= \frac{\{(p^2 - Q^2)p\}^3 + \{(2pQ + Q^2)Q\}^3 - \{(2pQ + Q^2)p\}^3 - \{(p^2 - Q^2)Q\}^3}{(p^2 + pQ + Q^2)^3} + Q^3$$

Let $$r = p^2 + pq + q^2 \text{ and } s = p^2 + pQ + Q^2.$$

Then
$$\{(p^2 - q^2)ps\}^3 + \{(2pq + q^2)qs\}^3 + \{2pQ + Q^2)pr\}^3$$
$$+ \{(p^2 - Q^2)rQ\}^3 + (rsq)^3$$
$$= \{(p^2 - Q^2)pr\}^3 + \{(2pQ + Q^2)Qr\}^3 + \{(2pq + q^2)ps\}^3$$
$$+ \{(p^2 - Q^2)qs\}^3 + (rsQ)^3$$

Hence a two-parameter solution of $2\cdot2$

Besides, if we further impose the conditions

$$p\ q\ o,\ P > Q > O$$

the solutions obtained will be in positive integers.

3·2 *Equation No.* $2\cdot3$:

$$x = a,\ y = b,\ z = C$$
$$X = A,\ Y = B,\ Z = c$$
$$a = p^2 - q^2, \quad b = 2pq, \quad c = p^2 + q^2$$
$$A = p^2 - Q^2, \quad B = 2pQ, \quad C = p^2 + Q^2$$

is a two-parameter solution of

$$x, y, z \overset{n}{=} X, Y, Z\ (n = 2, 4)$$

$$xy, yz, zx \overset{n}{=} XY, YZ, ZX\ (n = 2)$$

or when $a = p^2 - q^2, \quad b = 2pq, \quad c = p^2 + q^2$

$$A = p^2 - Q^2, \quad B = 2pQ, \quad C = p^2 + Q^2 \tag{1}$$

We obtain

$$\left.\begin{aligned} a^2 + b^2 &= c^2 \\ A^2 + B^2 &= C^2 \end{aligned}\right\} \tag{2}$$

$$ab = AB$$

Hence by squaring both sides of the equations (2), we find that

$$c^4 - a^4 - b^4 = 2a^2b^2 = 2A^2B^2 = C^4 - A^4 - B^4$$

so that

$$a^4 + b^4 + C^4 = A^4 + B^4 + c^4 \tag{3}$$

i.e., the values (1) satisfy (2) and (3) simultaneously and hence we obtain solutions of

$$x, y, z \overset{n}{=} X, Y, Z, \ (n = 2, 4) \tag{4}$$

The relation $xy, yz, zx = XY, YZ, ZX \ (n = 2)$ (4·1)

follows immediately from (4)

3·3 *Equation No.* 2·4

$$x_1 = x^2 + y^2, y_1 = y^2 + z^2, z_1 = z^2 + x^2$$

$$x_2 = \frac{-x^2 + y^2 + z^2}{2}, y_2 = \frac{x^2 - y^2 + z^2}{2}, z_2 = \frac{x^2 + y^2 - z^2}{2}$$

$$u = x, \quad v = y, \quad w = z$$

$$U = X, \quad V = Y, \quad W = Z$$

is a two-parameter solution of

$$x_i, y_i, z_i, u^2, v^2, w^2 \overset{n}{=} X_i, Y_i, Z_i, U^2, V^2, W^2 \ ; \ i = 1,2, \ n = 1, 2, 3$$

for from (4) and (4·1) we obtain that

$$x^2 + y^2, y^2 + z^2, z^2 + x^2, x^2, y^2, z^2 \overset{n}{=} X^2 + Y^2, Y^2 + Z^2, Z^2 + X^2, X^2, Y^2, Z^2 \quad (n = 1, 2)$$

$$\frac{-x^2 + y^2 + z^2}{2}, \frac{x^2 - y^2 + z^2}{2}, \frac{x^2 + y^2 - z^2}{2}, x^2, y^2, z^2, \overset{n}{=} \frac{-X^2 + Y^2 + Z^2}{2},$$

$$\frac{X^2 - Y^2 + Z^2}{2}, \frac{X^2 + Y^2 - Z^2}{2}, X^2, Y^2, Z^2 \ (n = 1, 2)$$

and because of the identities

$$(x^2 + y^2)^3 + (y^2 + z^2)^3 + (z^2 + x^2)^3 + x^6 + y^6 + z^6 = 3(x^2 + y^2 + z^2)(x^4 + y^4 + z^4)$$

$$\left(\frac{-x^2 + y^2 + z^2}{2}\right)^3 + \left(\frac{x^2 - y^2 + z^2}{2}\right)^3 + \left(\frac{x^2 + y^2 - z^2}{2}\right)^3 + x^6 + y^6 + z^6$$

$$= 3(x^2 + y^2 + z^2)(x^2 y^2 + y^2 z^2 + z^2 x^2) - (x^2 + y^2 + z^2)^3 \frac{}{2} - (x^2 + y^2 + z^2)^3$$

the following identities are satisfied.

$$(x^2+y^2)^3+(y^2+z^2)^3+(z^2+x^2)^3+x^6+y^6+z^6=(X^2+Y^2)^3+(Y^2+Z^2)^3+(Z^2+X^2)^3+X^6+Y^6+Z^6$$
$$\left(\frac{-x^2+y^2+z^2}{2}\right)^3+\left(\frac{x^2-y^2+z^2}{2}\right)^3+\left(\frac{x^2+y^2-z^2}{2}\right)^3+x^6+y^6+z^6$$
$$=\left(\frac{-X^2+Y^2+Z^2}{2}\right)^3+\left(\frac{X^2-Y^2+Z^2}{2}\right)^3+\left(\frac{X^2+Y^2-Z^2}{2}\right)^3+X^6+Y^6+Z^6 \quad (8)$$

Hence two-parameter solutions of the equations (2·4).

4. For the same values of p, q, Q given in (1) two-parameter solutions of the rest of the equations in 2 are enumerated as under :

2·1 $$x=q+p, \quad y=q-p, \quad z=2Q$$
$$X=Q+p, \quad Y=Q-p, \quad Z=2q.$$

2·5 $$x=h_1^2-k_1^2,\ h_1=h_2^2-k_2^2,\ h_2=h_3^2-k_3^2\ \ldots\ h_{n-1}=h_n^2-k_n^2$$
$$y=2h_1k_1+k_1^2,\ k_1=2h_2k_2+k_2^2,\ k_2=2h_3k_3+k_3^2,\ k_{n-1}=2h_nk_n+k_n^2$$

2·6 $$x=2q^2-p^2,\ y=Q^2,\ X=2Q^2-p^2,\ Y=q^2.$$

2·7 $$x=q^2-p^2,\ y=Q^2-p^2,\ X=p(Q^2-p^2),\ Y=p(q^2-p^2)$$

2·8 $$x_1=h^2+hk+k^2, \quad x_2=h(h+k), \quad x_3=k(h+k)$$
$$y_1=h+k \quad y_2=k \quad y_3=h$$
$$x_4=(p^2+q^2)(h+k) \quad y_4=(p^2+q^2)$$
$$X_1=u^2+uv+v^2 \quad X_2=u(u+v), \quad X_3=v(u+v)$$
$$Y_1=u+v,\ Y_2=u, \quad Y_3=v.$$
$$h=p^2-q^2, \quad k=2pq, \quad u=p^2-Q^2, \quad v=2pQ.$$

2·9 $$x=p^2+q^2,\ y=p^2-q^2,\ z=2pq\ ;\ X=p^2-Q^2,\ Y=p^2-Q^2,\ Z=2pQ.$$

2·91. $$X=h+k, \quad Y=k, \quad x=p, \quad y=Q, \quad z=u_n^2-v_n^2$$
$$h=u_1^2+v_1^2,\ k=2u_1v_1\ ;\ u_i=u_{i+1}^2+v_{i+1}^2,\ v_i=2u_{i+1}v_{i+1}\ (i=1,2\ldots n-1)$$

Acknowledgment

I am grateful to Professor Ganpathy Iyyer for having helped me in recasting the note in its present form.

Reference

1. Goodstein, R. L. *Gazette*, XXIII, 266, 1939.

Proc. Nat. Acad. Sci., India, 38(A), I & II 1968

On the derivative of the H-function

By

K. C. GUPTA & U. C. JAIN

M. R. Engg. College, Jaipur and University of Udaipur, Upaipur

[Received on 9th January, 1967]

Abstract

The aim of this paper is to obtain some formulae involving the rth derivative of the H-function with the help of operational Calculus. It is expected that the study of this note will reveal the utility of this useful branch of Mathematics in establishing in a systamatic manner certain interesting and general results.

1. Introduction

In this note we shall be concerned with the H-function introduced by Fox [(3), page 408]. This function will be defined and represented as follows :

$$H^{\,m,n}_{p,q}\left[x \,\middle|\, \begin{matrix}(a_1, \alpha_1), \ldots, (a_p, \alpha_p)\\ (b_1, \beta_1), \ldots, (b_q, \beta_q)\end{matrix}\right]$$

$$= \frac{1}{2\pi i}\int_L \frac{\prod_{1}^{m}\Gamma(b_j - \beta_j\xi)\ \prod_{1}^{n}\Gamma(1 - a_j + \alpha_j\xi)}{\prod_{m+1}^{q}\Gamma(1 - b_j + \beta_j\xi)\ \prod_{n+1}^{p}\Gamma(a_j - \alpha_j\xi)}\, x^{\xi} d\xi \qquad (1{\cdot}1)$$

where x is not equal to zero and an empty product is interpreted as unity ; p,q,m,n are integers satisfying $1 \leqslant m \leqslant q$; $0 \leqslant n \leqslant p$; $\alpha_j (j = 1, \ldots, p)$; $\beta_j (j = 1, \ldots, q)$ are positive numbers and $a_j (j = 1, \ldots, p)$; $b_j (j = 1, \ldots, q)$ are complex numbers, such that no pole of $\Gamma(b_h - \beta_h\xi)$ $(h = 1, \ldots, m)$ coincides with any pole of $\Gamma(1 - a_i + \alpha_i\xi)$ $(i = 1, \ldots, n)$ *i.e.*

$$\alpha_i(b_h + \nu) \neq \beta_i(a_i - \eta - 1) \qquad (1{\cdot}2)$$

$(\nu, \eta = 0, 1, \ldots ; h = 1, \ldots, m ; i = 1, \ldots, n)$

Further the contour L runs from $\sigma - i\infty$ to $\sigma + i\infty$ such that the points :

$$\xi = (b_h + \nu)/\beta_h \quad (h = 1, \ldots, m ; \nu = 0, 1, \ldots,) \qquad (1{\cdot}3)$$

which are poles of $\Gamma(b_h - \beta_h\xi)$ lie to the right and the points :

$$\xi = (a_i - \eta - 1)/\alpha_i \ (i = 1, \ldots, n ; \eta = 0, 1, \ldots ;) \qquad (1{\cdot}4)$$

which are poles of $\Gamma(1 - a_i + \alpha_i\xi)$ lie to the left of L. Such a contour is possible on account of (1·2).

2. We shall define and represent the classical Laplace transform by the following integral equation :

$$L\{f(x) ; s\} = \int_0^{\infty} e^{-sx} f(x)\, dx \qquad (2{\cdot}1)$$

provided that the integral on the R. H. S. is convergent.

The following results [(2), pages 129, 130 ; (4), eqs. 1.5.5; 1.7.5] will be required in the sequel :

$$(i) \qquad L\{x^n f(x) ; s\} = (-1)^n \frac{d^n}{ds^n}\left[L\{f(x) ; s\} \right] \tag{2·2}$$

$$(ii) \quad L\left\{ x^m \frac{d^n}{dx^n} f(x) ; s \right\} = \left(-\frac{d}{ds} \right)^m [\, s^n L\{f(x) ; s\} \,] \tag{2·3}$$

$$(ii) \quad L\left\{ x^l H^{\,m,\,n}_{\,p,\,q}\left[zx^\sigma \,\middle|\, \begin{matrix} (a_1, \alpha_1), \ldots, (a_p, \alpha_p) \\ (b_1, \beta_1), \ldots, (b_q, \beta_q) \end{matrix} \right] ; s \right\}$$

$$= s^{-l-1} H^{\,m,\,n+1}_{\,p+1,\,q}\left[zs^{-\sigma} \,\middle|\, \begin{matrix} (-l_1\, \sigma), (a_1, \alpha_1), \ldots, (a_p, \alpha_p) \\ (b_1, \beta_1), \ldots, (b_q, \beta_q) \end{matrix} \right] \tag{2·4}$$

provided that $R(s) > 0$, $\sigma > 0$, $R\left(l + 1 + \sigma \min \frac{b_h}{\beta_h} \right) > 0$ $(h = 1, \ldots, m)$,

$$\lambda = \sum_1^n (\alpha_j) - \sum_{n+1}^p (\alpha_j) + \sum_1^m (\beta_j) - \sum_{m+1}^q (\beta_j) > 0$$

and $\quad |\arg z| < \frac{1}{2}\lambda\pi.$

$$(iv) \; s^{-l-1} H^{\,m,\,n}_{\,p,\,q}\left[zs^{-\sigma} \,\middle|\, \begin{matrix} (a_1, \alpha_1), \ldots, (a_p, \alpha_p) \\ (b_1, \beta_1), \ldots, (b_q, \beta_q) \end{matrix} \right]$$

$$= L\left\{ x^l H^{\,m,\,n}_{\,p,\,q+1}\left[zx^\sigma \,\middle|\, \begin{matrix} (a_1, \alpha_1), \ldots, (a_p, \alpha_p) \\ (b_1, \beta_1), \ldots, (b_q, \beta_q), (-l, \sigma) \end{matrix} \right] ; s \right\} \tag{2·5}$$

provided that $R(s) > 0$, $\sigma > 0$, $R\left(l + 1 + \sigma \min \frac{b_h}{\beta_h} \right) > 0$ $(h = 1, \ldots, m)$

$(\lambda - \sigma) > 0$ and $|\arg z| < \frac{1}{2}(\lambda - \sigma)\pi$.

In what follows the following abbreviations will be used :

$\{ (a_p, \alpha_p) \}$ for $(a_1, \alpha_1), \ldots, (a_p, \alpha_p)$ and

$(a, \alpha)_r$ for $(a, \alpha), (a, \alpha), \ldots\ldots r$ times.

3. In this section we shall prove the following results. The conditions of validity of all these results being :

$\left(\lambda + \sigma \frac{b_h}{\beta_h} \right) > 0$ $(h = 1, \ldots, m)$ and the rth derivative of

$$x^\lambda H^{\,m,\,n}_{\,p,\,q}\left[zx^\sigma \,\middle|\, \begin{matrix} \{ (a_p, \alpha_p) \} \\ \{ (b_q, \beta_q) \} \end{matrix} \right] \text{ should exist.}$$

$$\frac{d^r}{dx^r}\left\{ x^\lambda H^{\,m,\,n}_{\,p,\,q}\left[zx^\sigma \,\middle|\, \begin{matrix} \{ (a_p, \alpha_p) \} \\ \{ (b_q, \beta_q) \} \end{matrix} \right] \right\}$$

$$= x^{\lambda - r} H^{\,m,\,n+1}_{\,p+1,\,q+1}\left[zx^\sigma \,\middle|\, \begin{matrix} (-\lambda, \sigma), \{ (a_p, \alpha_p) \} \\ \{ (b_q, \beta_q) \}, (-\lambda + r, \sigma) \end{matrix} \right] \tag{3·1}$$

$$\left(x\,\frac{d}{dx}\right)^r \left\{x^\lambda H\begin{matrix}m,\,n\\p,\,q\end{matrix}\left[z\,x^\sigma \,\middle|\, \begin{matrix}\{(a_p,\,\alpha_p)\}\\ \{(b_q,\,\beta_q)\}\end{matrix}\right]\right\}$$

$$= x^\lambda H\begin{matrix}m,\,n+r\\p+r,\,q+r\end{matrix}\left[z\,x^\sigma \,\middle|\, \begin{matrix}(-\lambda,\,\sigma)_r,\,\{(a_p,\,\alpha_p)\}\\ \{(b_q,\,\beta_q)\},\,(1-\lambda,\,\sigma)_r\end{matrix}\right] \tag{3·2}$$

$$\left(\frac{d}{dx}\,x\right)^r \left\{x^\lambda H\begin{matrix}m,\,n\\p,\,q\end{matrix}\left[z\,x^\sigma \,\middle|\, \begin{matrix}\{(a_p,\,\alpha_p)\}\\ \{(b_q,\,\beta_q)\}\end{matrix}\right]\right\}$$

$$= x^\lambda H\begin{matrix}m,\,n+r\\p+r,\,q+r\end{matrix}\left[z\,x^\sigma \,\middle|\, \begin{matrix}-\lambda-1,\,\sigma)_r,\,\{(a_p,\,\alpha_p)\}\\ \{(b_q,\,\beta_q)\},\,(-\lambda,\,\sigma)_r\end{matrix}\right] \tag{3·3}$$

$$\left(\frac{1}{x}\,\frac{d}{dx}\right)^r \left\{x\lambda H\begin{matrix}m,\,n\\p,\,q\end{matrix}\left[z\,x^\sigma \,\middle|\, \begin{matrix}\{(a_p,\,\alpha_p)\}\\ \{(b_q,\,\beta_q)\}\end{matrix}\right]\right\}$$

$$= x^{\lambda-2r} H\begin{matrix}m,\,n+r\\p+r,\,q+r\end{matrix}\left[z\,x^\sigma \,\middle|\, \begin{matrix}(-\lambda,\,\sigma),\ldots,(-\lambda+2r-2,\,\sigma),\{(a_p,\,\alpha_p)\}\\ \{(b_q,\,\beta_q)\},\,(1-\lambda,\,\sigma),\ldots,(2r-1-\lambda,\,\sigma)\end{matrix}\right] \tag{3·4}$$

$$\left(\frac{d}{dx}\cdot\frac{1}{x}\right) \left\{x^\lambda H\begin{matrix}m,\,n\\p,\,q\end{matrix}\left[z\,x^\sigma \,\middle|\, \begin{matrix}\{(a_p,\,\alpha_p)\}\\ \{(b_q,\,\beta_q)\}\end{matrix}\right]\right\}$$

$$= x^{\lambda-2r} H\begin{matrix}m,\,n+r\\p+r,\,q+r\end{matrix}\left[z\,x^\sigma \,\middle|\, \begin{matrix}(1-\lambda,\,\sigma),\ldots,(2r-1-\lambda,\,\sigma),\{(a_p,\,\alpha_p)\}\\ \{b_q,\,\beta_q)\},\,(2r-\lambda,\,\sigma),\ldots,(2-\lambda,\,\sigma)\end{matrix}\right] \tag{3·5}$$

Proofs : To prove (3·1), we take

$$f(x) = x^\lambda H\begin{matrix}m,\,n\\p,\,q\end{matrix}\left[z\,x^\sigma \,\middle|\, \begin{matrix}\{(a_p,\,\alpha_p)\}\\ \{(b_q,\,\beta_q)\}\end{matrix}\right]$$

in the R. H. S. of (2·3). Then by virtue of (2·4) its value reduced to the following expression :

$$\left(-\frac{d}{ds}\right)^R \left\{s^{r-\lambda-1} H\begin{matrix}m,\,n+1\\p+1,\,q\end{matrix}\left[z\,x^{-\sigma} \,\middle|\, \begin{matrix}(-\lambda,\,\sigma),\{(a_p,\,\alpha_\rho)\}\\ \{(b_q,\,\beta_q)\}\end{matrix}\right]\right\} \tag{A}$$

Taking the inverse Laplace transform of the quantity within the crooked bracket in (*A*) with the help of (2·5) and then applying (2·2) in the result thus obtained, R. H. S. of (2·3) becomes equal to :

$$L\left\{x^{\lambda-r+R} H\begin{matrix}m,\,n+1\\p+1,\,q+1\end{matrix}\left[z\,x^\sigma \,\middle|\, \begin{matrix}(-\lambda,\,\sigma),\{(a_p,\,\alpha_p)\}\\ \{(b_q,\,\beta_q)\},\,(r-\lambda,\sigma)\end{matrix}\right];s\right\} \tag{B}$$

Therefore (2·3) is equivalent to

$$L\left[x^R\frac{d^r}{dx^r}\left\{x^\lambda H\begin{matrix}m,\,n\\p,\,q\end{matrix}\left[z\,x^\sigma \,\middle|\, \begin{matrix}\{(a_p,\,\alpha_p)\}\\ \{(b_q,\,\beta_q)\}\end{matrix}\right]\right\};s\right]$$

$$= L\left[x^{\lambda-r+R} H\begin{matrix}m,\,n+1\\p+1,\,q+1\end{matrix}\left[z\,x^\sigma \,\middle|\, \begin{matrix}(-\lambda,\,\sigma),\{(a_p,\,\alpha_p)\}\\ \{(b_q,\,\beta_q)\},\,(r-\lambda,\,\sigma)\end{matrix}\right];s\right] \tag{3·6}$$

Interpreting (3·6) with the help of Lerch's theorem [5] which states that every function has got a unique image in the Laplace transform, we arrive at (3·1).

The results (3·2) to (3·5) can easily be proved by successive application of (3·1).

On account of the general nature of the H-function the results (3·1) to (3·5) can be used as key formulae for obtaining the *r*th derivative of the various important special functions occurring in applied Mathematics *viz.* Meijer's G-function, Maitland's generalized hypergeometric and Bessel functions, MacRobert's E-function, Bessel function etc. We shall however for lack of space specify the particular cases of the H-function in terms of the Meijer's G–function only.

Thus if we take $\sigma = 1$, and all α's and β's equal to unity in (3·1), the H-function break up into G-function and we get all the results obtained recently by Bhise [(1) pages 350, 351].

Acknowledgements

The authors are thankful to Dr. K. C. Sharma for his keen interest in the preparation of this paper and to the referee for making a useful suggestion.

References

1. Bhise, V. M. On the derivative of Meijer's G–function and MacRobert's E-function. *Proc. Nat. Acad. Sci. India*, **32** : 349–354, 1962.
2. Erdelyi, A. *et al.* Tables of integral transforms, **Vol. I** : (McGraw-Hill, New York, 1954.
3. Fox, C. The G and H-functions as symmetrical Fourier kernels. *Trans. Amer. Math. Soc.*, **98** : 395-429, 1961.
4. Gupta, K. C. A study of Meijer transforms, thesis approved for Ph.D. degree. *Univ. Raj. India*, 1966.
5. Lerch, E. Sur Un point de la theorie des functions generatrices d'Abel. *Acta. Math.*, **27** : 339, 1903.

Proc. Nat Acad. Sci., India, 38(A), I & II, 1968.

On Self-Reciprocal Functions

By

D. G. JOSHI

Department of Mathematics, Holkar Science Collegc, Indore

[Received on 10th January, 1967]

Abstract

In this paper conditions are obtained for a particular class of functions to be self-reciprocal in any transform having a symmetrical Fourier kernel as its kernel. Further, this property is used in establishing two theorems. These theorems give the form of a Transforming Kernel, transforming a self-reciprocal function in one transform to another function self-reciprocal in other transform. Theorems are illustrated by examples.

1. Hardy and Titchmarsh [5, pages 198, 200] have established theorems giving necessary and sufficient conditions for a function, $f(x)$, to be self-reciprocal in Fourier Cosine, Fourier Sine and Hankel transforms, for certain class of functions. Similar theorems have been established by different workers for particular transforms *e. g.* $\chi_{\nu,k,m}$ – transform [7, page 283] transform defined by Bhatnagar [1, page 99] and transform defined by Verma [11, page 34]. The similarity of conditions of self-reciprocal functions in different reciprocal transforms suggest that, there is a property of Fourier kernels, which is streaming in all these kernels and that these theorems are simply the particular cases of this property. In section 2, this property is establishing and used in following sections. In 3, conditions for self-reciprocal functions are obtained and illustrated by an example in 4. Two theorems are established giving form of transforming kernels in 5. Transforming kernels are constructed in section 6 and in the last section one of them is used to transform one self-reciprocal function into another.

2. If $k(x)$ is a Fourier kernel, $K(s)$ is its Mellin transform defined by the equation

$$K(s) = \int_0^\infty k(xy)\, f(y)\, dy \tag{2·1}$$

and the transform of $f(y)$, given by the equation

$$g(x) = \int_0^\infty k(xy)\, f(y)\, dy \tag{2·2}$$

then we have [6, page 117]

$$K(s)\, K(1-s) = 1 \tag{2·3}$$

If $K(s)$ is as in (2·1) and is $O(1)$, then it is possible to put $K(s)$ in the form

$$K(s) = \frac{K_1(s)}{K_1(1-s)} \tag{2·4}$$

where $K_1(s)$ is of some order, say $O(e^{\lambda t})$ and $s = \sigma + it$

Recently [4] Fox has also divided the Mellin transform of a kernel function in the form of a G-function in one of his theorems.

3. *Theorem* 1 :

A necessary and sufficient condition that a function, $f(x)$, of $A(a, a)$ [3, page 252], should be its own k-transform, where $k(x)$, the kernel function of the transform is such that its Mellin transform, $K(s)$, is $O(1)$, $K_1(s)$ is $O(e^{\lambda|t|})$ and satisfies the relation (2·4) is that $f(x)$ should be of the form

$$f(x) = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} K_1(s)\,\psi(s)\,x^{-s}\,ds \tag{3·1}$$

with

$$\psi(s) = \psi(1-s) \tag{3·2}$$

where $\psi(s)$ and $K_1(s)$ are regular in the strip (3·3)

$$a < \sigma < 1 - a, \quad a < \tfrac{1}{2}$$

$$\psi(s) \text{ is } O(e^{(-\lambda-a+\eta)|t|}).$$

for every positive η and uniformly in the strip (3·3) and c is any value of σ in the strip (3·3)

Proof:

To prove that the condition is necessary.

As $f(x)$ belongs to $A(a, a)$, its Mellin transform, $F(s)$ exists [3, page 47], it is regular in the strip (3·3) and is $O(e^{(-a+\eta)|t|})$ for every positive η and uniformly in the strip (3·3).

Thus we have

$$F(s) = \int_0^\infty f(x)\,x^{s-1}\,dx \tag{3·4}$$

Because $f(x)$ is self-reciprocal in k-transform, we have

$$F(s) = \int_0^\infty x^{s-1}\left[\int_0^\infty k(xy)\,f(y)\,dy\right]dx$$

Changing the order of integration, which is valid [2, page 504], provided $\int_0^\infty k(xy)\,f(y)\,dy$ is absolutely convergent and Mellin transform of $|f(x)|$ exists, we have from (2·1) and (3·4)

$$F(s) = K(s)\,F(1-s) \tag{3·5}$$

Using (2·4),

$$\frac{F(s)}{F(1-s)} = \frac{K_1(s)}{K_1(1-s)}$$

Putting

$$F(s) = K_1(s)\,\psi(s) \tag{3·6}$$

we observe that

$$\psi(s) = \psi(1-s)$$

As $F(s)$ is regular in the strip (3·3), so are $K_1(s)$ and $\psi(s)$ in (3·3). Because $K_1(s)$ is $O(e^{\lambda|t|})$, so $\psi(s)$ is $O(e^{(-a-\lambda+\eta)|t|})$. Taking Mellin inverse from (3·6), we have

$$f(x) = \frac{1}{2\pi i}\int_{c+i\infty}^{c+i\infty} K_1(s)\,\psi(s)\,x^{-s}\,ds.$$

Sufficiency of the conditions can be proved similar to corresponding theorem of cosine transform [3, page 252].

4. We now show that the conditions obtained for self-reciprocal functions in different transforms follow as particular cases of our theorem.

If

$$k(x) = 2\beta\gamma\, x^{\gamma-\frac{1}{2}}\; G^{\,q\;\;p}_{2p\,2q}\left(\beta^2x^2 \,\middle|\, \begin{matrix} a_1, \ldots\ldots a_p\,; -a_1, \ldots\ldots -a_p \\ b_1, \ldots\ldots b_q\,; -b_1, \ldots\ldots -b_l \end{matrix}\right)$$

with β and γ as real constants, the kernal obtained by R. Narain [8, page 951] then

$$K(s) = \frac{\beta^{1/2\gamma-s/\gamma}\prod_{j=1}^{q}\Gamma\left(\frac{2\gamma-1}{4\gamma}+b_j+\frac{s}{2\gamma}\right)\prod_{j+1}^{p}\Gamma\left(\frac{2\gamma+1}{4\gamma}-a_j-\frac{s}{2\gamma}\right)}{\prod_{j+1}^{q}\Gamma\left(\frac{2\gamma+1}{4\gamma}+b_j-\frac{s}{2\gamma}\right)\prod_{j=1}^{p}\Gamma\left(\frac{2\gamma-1}{4\gamma}-a_j+\frac{s}{2\gamma}\right)}$$

From (2·4) we have

$$K_1(s) = \frac{\beta^{-s/2\gamma}\prod_{j=1}^{q}\Gamma\left(\frac{2\gamma-1}{4\gamma}+b_j+\frac{s}{2\gamma}\right)}{\prod_{j=1}^{p}\Gamma\left(\frac{2\gamma-1}{4\gamma}-a_j+\frac{s}{2\gamma}\right)}$$

and $K_1(s)$ is $O(e^{-\frac{\pi}{4\gamma}(q-p)|t|})$

From the theorem a self-reciprocal function, $f(x)$, in this transform should be of the form [10]

$$f(x) = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty}\beta^{-s/2\gamma}\,\frac{\prod_{j=1}^{q}\Gamma\left(\frac{2\gamma-1}{4\gamma}+b_j+\frac{s}{2\gamma}\right)}{\prod_{j=1}^{p}\Gamma\left(\frac{2\gamma-1}{4\gamma}-a_j+\frac{s}{2\gamma}\right)}\,\psi(s)\,x^{-s}\,ds$$

where $\psi(s)$ is $O(e^{\left\{\frac{\pi}{4\gamma}(\gamma-p)-a+\eta\right\}|t|})$, regular in the strip (3·3) and satisfies (3·2).

On specialising the parameters we can obtain forms of function, self-reciprocal in different transform like $\chi_{\nu,k,m}$ – transform, [7, page 284] transform defined by Bhatnagar [1, page 99] etc.

5. *Theorem* 2 :

A necessary and sufficient condition for a kernel, $T(x)$, transforming a self-reciprocal function, $f(x)$, of class $A(a, a)$, in k-transform to another function, $g(x)$, self-reciprocal in h-transform with the help of a relation.

$$g(x) = \int_0^\infty T(xy)\,f(y)\,dy \qquad (5\cdot1)$$

is that the kernel, $T(x)$, should be of the form

$$T(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} K_1(s)\ H_1(s)\ \omega(s)\ x^{-s}\ ds \tag{5·2}$$

with

$$\omega(s) = \omega(1-s) \tag{5·3}$$

where

$$\frac{K_1(s)}{K_1(1-s)} = K(s),\ \frac{H_1(s)}{H_1(1-s)} = H(s) \tag{5·4}$$

$K(s)$ and $H(s)$ being the Mellin transforms of $k(x)$ and $h(x)$,

$$K_1(s) = O(e^{\lambda_1|t|}),\ H_1(s) = O(e^{\lambda_2|t|}),$$
$$w(s) = O(e^{(-\lambda_1-\lambda_2-\alpha+\eta)|t|}) \tag{5·5}$$

for every positive η and uniformly in the strip

$$a < \sigma < 1-a,\quad a < \tfrac{1}{2} \tag{5·6}$$

c in any value of σ in the strip (5·6)

Proof:

(a) To prove that the condition is necessary.

Under the conditions of the theorem the Mellin transforms $F(s)$, $G(s)$, and $T(s)$ of $f(x)$, $g(x)$ and $T(x)$ exist and hence from (5·1) we have

$$G(s) = T(s)\ F(1-s) \tag{5·7}$$

As $f(x)$ and $g(x)$ are self-reciprocal in k and h-transforms respectively we can write as in theorem 1.

$$F(s) = K_1(s)\ \psi_1(s),\ G(s) = H_1(s)\ \psi_2(s) \tag{5·8}$$

where $\psi_1(s) = \psi_1(1-s),\ \psi_2(s) = \psi_2(1-s)$

Using these relations in (5·7)

$$T(s) = \frac{H_1(s)\ \psi_2(s)}{K_1(1-s)\ \psi_1(1-s)}$$

which takes the form

$$T(s) = H_1(s)\ K_1(s)\ \omega(s) \tag{5·9}$$

where $\omega(s) = \psi_2(s)/K_1(s)\ K_1(1-s)\ \psi_1(1-s) = \omega(1-s)$

Taking Mellin inverse of (5·9)

$$T(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} H_1(s)\ K_1(s)\ \omega(s)\ x^{-s}\ ds \tag{5·10}$$

with $\omega(s) = \omega(1-s)$

(*b*) To prove that the condition is sufficient.

Substituting the value of $T(x)$ from (5·2) in (5·1) we have

$$g(x) = \int_0^\infty f(y) \left[\frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} H_1(s)\, K_1(s)\, \omega(s)\, (xy)^{-s}\, ds \right] dy$$

Changing the order of integration, which is assumed to be permissible and evaluating the y – integral, we have

$$g(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} H_1(s)\, K_1(s)\, \omega(s)\, F(1-s)\, x^{-s}\, ds.$$

Using (5·8)

$$g(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} H_1(s)\, K_1(s)\, \omega(s)\, K_1(1-s)\, \psi_1(1-s)\, x^{-s}\, ds$$

with $$\omega_1(s) = K_1(s)\, K_1(1-s)\, \omega(s)\, \psi_1(1-s)$$

$$g(x) = \frac{1}{2\pi i} \int_{c-i\infty}^{c+i\infty} H_1(s)\, \omega_1(s)\, x^{-s}\, ds$$

where $$\omega_1(s) = \omega_1(1-s)$$

Because of (3·1) $g(x)$ is self-reciprocal in h–transform.

As the transforming kernel, $T(x)$, in (5·2) is symmetric with respect to $K_1(s)$ and $H_1(s)$, it also transforms a function self-reciprocal in h-transforms to that in k-transform.

By assuming different forms of the transforming kernel, $T(x)$, we can establish different theorems, like theorem 2. If the self-reciprocal function $f(x)$ and $g(x)$ are connected by the kernel, $T(x)$, in the form $\frac{1}{x}\, T\left(\frac{y}{x}\right)$, instead of $T(xy)$ in (5·1), using the relation

$$g(x) = \frac{1}{x} \int_0^\infty T\left(\frac{y}{x}\right) f(y)\, dy$$

with its Mellin transform

$$G(s) = F(s)\, T(1-s)$$

we have the theorem given below which can be proved by proceeding on lines similar to those followed in theorem 2.

Theorem 3 :

If $f(x)$, of $A(a,\ a)$, is self-reciprocal in k–transform, then the transforming kernel, $T(x)$ which transforms a function $f(x)$, self-reciprocal in k-transform to a self-reciprocal function, $g(x)$, in h-transform, with the help of equation.

$$g(x) = \frac{1}{x} \int_0^\infty T\left(\frac{y}{x}\right) f(y)\, dy$$

is that, $T(x)$, should be of the form

$$T(x) = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} H_1(1-s)\, K_1(s)\, \omega(s)\, x^{-s}\, ds$$

with $\omega(s) = \omega(1-s)$

where $K_1(s)$ and $H_1(s)$ are as defined in theorem 2.

Because this kernel is not symmetric in $K_1(s)$ and $H_1(s)$, so it does not transform a self-reciprocal function in h-transform to a function self-reciprocal in k-transform.

5.1. *Particular Cases* :

If the kernel functions $k(x)$ and $h(x)$ are selected from the same transform, but with different parameters then we shall obtain from the theorems, transforming kernels, changing a function self-reciprocal in the transform to another one with different parameters.

We give below a result which follow from the theorems and is known.

If $k(x) = x^{\frac{1}{2}} J_\mu(x)$, $h(x) = x^{\frac{1}{2}} J_\nu(x)$

then $K_1(s) = 2^{s/2}\,\Gamma(\frac{1}{4} + \frac{\mu}{2} + \frac{s}{2})$, $H_1(s) = 2^{s/2}\,\Gamma(\frac{1}{4} + \frac{\nu}{2} + \frac{s}{2})$

Thus from theorem 2, the transforming kernel changing R_μ to R_ν and *vise versa* will be of the form

$$T(x) = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} 2^s\,\Gamma(\tfrac{1}{4} + \tfrac{\mu}{2} + \tfrac{s}{2})\,\Gamma(\tfrac{1}{4} + \tfrac{\nu}{2} + \tfrac{s}{2})\,\omega(s)\,x^{-s}\,ds$$

with $\omega(s) = \omega(1-s)$

This is Rule 2 [3, page 268].

Similarly the transforming kernel changing R_μ to R_ν from theorem 3 will be of the form

$$T(x) = \frac{1}{2\pi i}\int_{c-i\infty}^{c+i\infty} 2^{\frac{1}{2}}\,\Gamma(\tfrac{1}{4} + \tfrac{\mu}{2} + \tfrac{s}{2})\,\Gamma(\tfrac{3}{4} + \tfrac{\nu}{2} - \tfrac{s}{2})\,\omega(s)\,x^{-s}\,ds$$

with $\omega(s) = \omega(1-s)$

Further if $\omega(s) = \xi\,\chi(s)$ where $\chi(s) = \chi(1-s)$

we have (9·15·3) of Rule 3 [3, page 270].

Similar rules can be derived by selecting different kernels functions and applying theorems 2 and 3.

6. Now we will obtain transforming kernels changing a self-reciprocal function in one transform to a function, self-reciprocal in other transform by selecting different kernel functions and using theorems 2 and 3.

We shall say that $g(y)$ is the G-transform of $f(y)$ when in (2·2)

$$k(x) = 2\,\beta\gamma x^{\gamma-\frac{1}{2}}\, G^{\,q\,p}_{2p\,2q}\left(\beta^2x^2 \,\middle|\, \begin{matrix} a_1, \ldots . a_p\,; -a_1, \ldots - a_p \\ b_1, \ldots . b_q\,; -b_1, \ldots - b_q \end{matrix}\right) \qquad (6\cdot1)$$

a kernel function [8, page 951] with β, γ as real constants. Further if $g(y) = f(y)$, then $f(y)$ will be called self-reciprocal in G-transform.

Transforming kernels :

If $$h(x) = x^{\frac{1}{2}} J_\mu (x)$$

and $$k(x) = G(x) \text{ as in } (6{\cdot}1)$$

then $$H_1(s) = 2^{s/2}\, \Gamma\left(\tfrac{1}{4} + \tfrac{\mu}{2} + \tfrac{s}{2}\right)$$

$$K_1(s) = \frac{\beta^{-s/2\gamma} \prod_{j=1}^{q} \Gamma\left(\frac{2\gamma - 1}{4\gamma} + b_j + \frac{s}{2\gamma}\right)}{\prod_{j=1}^{p} \Gamma\left(\frac{2\gamma - 1}{4\gamma} - a_j + \frac{s}{2\gamma}\right)}$$

From theorem 2, the transforming kernel transforming a R_μ function to a function self-reciprocal as in G-transform and *vice versa* is given by

$$\frac{1}{2\pi i}\int_L \frac{\beta^{-s/2\gamma}\, 2^{s/2}\, \Gamma\left(\frac{1}{4} + \frac{\mu}{2} + \frac{s}{2}\right) \prod_{j=1}^{q} \Gamma\left(\frac{2\gamma-1}{4\gamma} + b_j + \frac{s}{2\gamma}\right)}{\prod_{j=1}^{p} \Gamma\left(\frac{2\gamma-1}{4\gamma} - a_j + \frac{s}{2\gamma}\right)} \omega(s)\, x^{-s}\, ds$$

with $$\omega(s) = \omega(1-s)$$

Putting $\frac{s}{2\gamma} = S$, $(x^{2\gamma}\, \beta/2^{\gamma}) = \chi$ and $\omega(2\gamma s) = 1/2\gamma$, the kernel reduced to the form

$$T(\chi) = \frac{1}{2\pi i}\int_L \frac{\prod_{j=1}^{q} \Gamma\left(\frac{2\gamma-1}{4\gamma} + b_j + S\right)\, \Gamma\left(\frac{1}{4} + \frac{\mu}{2} + \gamma S\right)}{\prod_{j=1}^{p} \Gamma\left(\frac{2\gamma-1}{4\gamma} - a_j + S\right)} \chi^{-S}\, dS. \quad (6{\cdot}2)$$

Using the definition of H-function [4, page 408], the transforming kernel becomes

$$H^{q+1,\,0}_{p,\,q+1}\left[\frac{x^{2\gamma}\,\beta}{2^{\gamma}} \;\middle|\; \begin{matrix} ; \left(\frac{2\gamma - 1}{4\gamma} - a_1,\, 1\right), \ldots\ldots\ldots\ldots, \left(\frac{2\gamma-1}{4\gamma} - a_p,\, 1\right) \\ \left(\frac{2\gamma - 1}{4\gamma} + b_1,\, 1\right), \ldots., \left(\frac{2\gamma-1}{4\gamma} + b_q,\, 1\right), \left(\frac{\mu}{2} + \frac{1}{4},\, \gamma\right) \end{matrix}\right] \quad (6{\cdot}3)$$

where $\gamma > 0$, all the poles of the integrand of (6·2) are simple, the contour L is a straight line parallel to imaginary axis is the S $(s = \sigma + it)$ plane and the poles of $\Gamma\left(\frac{2\gamma-1}{4\gamma} + b_j + S\right)$ $[j = 1, 2 \ldots, q]$ and $\Gamma\left(\frac{\mu}{2} + \frac{1}{4} + \gamma S\right)$ lie on the left of L and $q + \gamma > 0$.

Further if we assume that γ is a positive integer, then by using multiplication formula for Gamma function, the H-function can be reduced to a G-function and transforming kernel (6·3) assumes the form.

$$(2\pi)^{\frac{1-\gamma}{2}} \gamma^{\frac{\mu}{2}-\frac{1}{4}} G^{q+\gamma,\,0}_{p,\,q+\gamma}\left(\frac{x^{2\gamma}\beta}{2^{\gamma}\gamma^{\gamma}}\,\middle|\,\begin{matrix}\frac{2\gamma-1}{4\gamma}-a_1,\ldots,\frac{2\gamma-1}{4\gamma}-a_p\\ \frac{2\gamma-1}{4\gamma}+b_1,\ldots,\frac{2\gamma-1}{4\gamma}+b_q,\ \Delta\left(\gamma,\frac{\mu}{2}+\frac{1}{4}\right)\end{matrix}\right) \tag{6·4}$$

Giving suitable values to the parameters in (6·4) we can obtain kernels, transforming R_μ to functions, self-reciprocal in different transform, *e.g.*

(*a*) Selecting $\beta=\frac{1}{2}$, $\gamma=1$, $p=1$, $q=2$, $a_1=-\frac{1}{2}-\frac{\nu}{2}+k-m$, $b_1=\frac{\nu}{2}+2m$ and $b_2=\frac{\nu}{2}$, the kernel reduces to

$$G^{3,\,0}_{1,\,3}\left(\frac{x^2}{4}\,\middle|\,\begin{matrix};\ \frac{\nu}{2}+\frac{3}{4}+m-k\\ \frac{\mu}{2}+\frac{1}{4},\frac{1}{4}+\frac{\nu}{2}+m\pm m\end{matrix}\right)$$

which transforms functions self-reciprocal in Hankel transform to functions self-reciprocal in $\chi_{\nu;k,m}$ - transform [7, p. 270].

Similarly using Theorem 3, another set of transforming kernels changing R_μ to a function self-reciprocal in G-transform is given by

$$\frac{1}{2\pi i}\int_L \frac{2^{s/2}\,\Gamma\left(\frac{1}{4}+\frac{\mu}{2}+\frac{s}{2}\right)\beta^{-(1-s)/2\gamma}\prod_{j=1}^{q}\Gamma\left(\frac{2\gamma-1}{4\gamma}+b_j+\frac{1-s}{2\gamma}\right)}{\prod_{j=1}^{p}\Gamma\left(\frac{2\gamma-1}{4\gamma}-a_j+\frac{1-s}{2\gamma}\right)}\,\omega(s)\,x^{-s}\,ds \tag{6·5}$$

which becomes

$$H^{1,\,q}_{q,\,q+1}\left[\frac{x^{2\gamma}}{2^{\gamma}\beta}\,\middle|\,\begin{matrix}\left(\frac{2\gamma+1}{4\gamma}+b_1,\,1\right),\ldots\ldots\ldots,\left(\frac{2\gamma+1}{4\gamma}+b_q,\,1\right)\\ \left(\frac{\mu}{2}+\frac{1}{4},\gamma\right);\left(\frac{2\gamma+1}{4\gamma}-a_1,\,1\right),\ldots,\left(\frac{2\gamma+1}{4\gamma}-a_p,\,1\right)\end{matrix}\right] \tag{6·6}$$

$(\gamma-q)>0$ and with similar assumptions as in (6·3).

Giving suitable values to the parameters we can obtain kernels transforming R_μ to a function self-reciprocal in different transforms, *e.g.*

Selecting $\beta=\frac{1}{2}$, $\gamma=1$, $p=1$, $q=2$, $a_1=-\frac{1}{2}-\frac{\nu}{2}+k-m$, $b_1=\frac{\nu}{2}+2m$ and $b_2=\frac{\nu}{2}$, the kernel reduces to

$$G^{1,\,2}_{2,\,2}\left(x^2\,\middle|\,\begin{matrix}\frac{3}{4}+\frac{\nu}{2}+2m,\ \frac{3}{4}+\frac{\nu}{2};\\ \frac{\mu}{2}+\frac{1}{4};\ \frac{5}{4}+\frac{\nu}{2}+m-k\end{matrix}\right)$$

which transforms R_μ to $R_\nu(k,m)$.

7. Now we shall obtain a function self-reciprocal in G-transform from a known R_μ function, with help of a transforming kernel.

Consider a R_μ – function [12, page 141]

$$x^{\mu-2\lambda-\frac{1}{2}}\, G^{3,\,2}_{2,\,3}\left(\frac{x^2}{2}\,\middle|\, \begin{matrix}\frac{1}{2}+\lambda-\frac{\mu}{2},\ 3\lambda-\mu+\frac{1}{2}\\ \frac{1}{2}+\lambda-\frac{\mu}{2},\ \frac{1}{2}+\lambda,\ \frac{1}{2}-\lambda\end{matrix}\right) \tag{7·1}$$

Using Theorem 2, $f(x)$ from (7·1) and the transforming kernel from (6·4) we have by using the integral [9, page 401]

$$g(y) = (2\pi)^{\beta(1-\gamma)}\,\gamma^{2\mu-4\lambda}\,2^{\frac{\mu}{2}-\lambda-\frac{3}{4}}\; G^{q+3\gamma,\,3\gamma}_{p+3\gamma,\,q+3\gamma}\left(\beta y^{2\gamma}\,\middle|\, \begin{matrix}\Delta(\gamma,\tfrac{1}{4}),\ \Delta(\gamma,\tfrac{1}{4}-\frac{\mu}{2}),\ \Delta(\gamma,\tfrac{1}{4}+2\lambda-\frac{\mu}{2});\ \left(\frac{2\gamma-1}{4\gamma}-a_1\right),\ldots.\left(\frac{2\gamma-1}{4\gamma}-a_p\right)\\ \Delta(\gamma,\tfrac{1}{4}),\ \Delta(\gamma,\tfrac{1}{4}+\frac{\mu}{2}),\ \Delta(\gamma,\tfrac{1}{4}\cdot 2\lambda+\frac{\mu}{2}),\ \left(\frac{2\gamma-1}{4\gamma}+b_1\right),\ldots.\left(\frac{2\gamma-1}{4\gamma}+b_q\right)\end{matrix}\right) \tag{7·2}$$

$2\gamma\, Re(b_j) > -(\gamma+1)$, $2\, Re(\gamma\, b_j+\mu/2) > -(\gamma+1)$, $2\, Re(\gamma\, b_j+\frac{\mu}{2}-2\lambda) > -(\gamma+1)$

$[j=1,\ldots q]$, $Re(\mu) > -1$, $Re(\mu-2\lambda) > -1$, $q+\gamma > p$ and $|\arg y| < (q+\gamma-p)\,\pi/4\gamma$

Giving particular values to the parameters in (7·2) we get self-reciprocal functions in different transforms, *e.g.*

If

$$\gamma=1,\ \beta=\tfrac{1}{2},\ p=1,\ q=2,\ a_1=-\tfrac{1}{2}-\tfrac{\nu}{2}+k-m,\ b_1=\tfrac{\nu}{2}+2m,\ b_2=\tfrac{\nu}{2}.$$

we have

$$g(y)=2^{\frac{\mu}{2}-\lambda-3/4}\; G^{5,\,3}_{4,\,5}\left(\frac{y^2}{2}\,\middle|\, \begin{matrix}\frac{1}{4},\ \frac{1}{4}-\frac{\mu}{2},\ \frac{1}{4}+2\lambda-\frac{\mu}{2};\ \frac{3}{4}+\frac{\nu}{2}+m-k\\ \frac{1}{4},\ \frac{1}{4}+\frac{\mu}{2},\ \frac{1}{4}-2\lambda+\frac{\mu}{2},\ \frac{1}{4}+\frac{\nu}{2}+2m,\ \frac{1}{4}+\frac{\nu}{2}\end{matrix}\right)$$

$Re(\mu) > -1$, $Re(\mu-2\lambda) > -1$, $Re(\mu-4\lambda) > -\frac{5}{4}$, $Re(\mu+\nu-4\lambda) > -\frac{5}{2}$

$Re(\mu+\nu+4m-4\lambda) > -\frac{5}{2}$, $Re(\mu+\nu) > -\frac{5}{2}$ and $|\arg y| < \pi/2$

This is clearly $R_\nu(k, m)$ [7, page 286]

Acknowledgements

My sincere thanks are due to Dr. V. M. Bhise, Shri G. S. Technological Institute, Indore for his help and guidence during the preparation of this paper. I am also thankful to Dr. S. M. Das Gupta, Principal, G. S. Technological Institute for the facilities he gave me.

References

1. Bhatnagar, K. P. *Ganit*, **4** : 99, 1953.
2. Bromwich. Theory of Infinite Series. *Edition*, 1925.
3. Titchmarsh, E. C. Introduction to the Theory of Fourier Integrals. *Edition*, 1948.
4. Fox, Charles. The G and H functions as symmetrical Fourier Kernels. *Trans. Amer. Math. Soc.*, **98** : 395 421, 1961.
5. Hardy and Titchmarsh. Self-Reciprocal Functions. *Quart. Journ. of Math.* (*Oxford*), **1** : 196-231, 1930.
6. Hardy and Titchmarsh. A Class of Fourier Kernels. *Proc. Camb. Philo. Soc.*, **35** (2) : 116-155, 1933.
7. Roop, Narain. On a Generalisation of Hankel Transform and Self-Reciprocal Functions. *Rendi. Semi. Mat. Torino*, **16** : 269-300, 1956-57.
8. Roop, Narain. The G functions as Unsymmetrical Fourier Kernels I. *Proc. Amer. Math. Soc.*, **13** (6) : 950-959, 1962.
9. Saxena, R. K. Some theorems on generalised Laplace Transform I. *Nat. Inst. Sci. India*, **26 A** (4): 401-413, 1960.
10. Sharma, O. P. On Self-Reciprocal Functions. *to appear in the Proc. Nat. Acad. of Sci. India, Allahabad.*
11. Varma, V. K. On a new Transform. *Ganit*, **10** (1) : 31 47, 1959.
12. Verma, C. B. L. G-function and Self-Reciprocity. *Proc. Nat. Acad. Sci. India*, **36A** (2) : 139-146, 1964.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968

On q-Polynomials

By

P. N. SHRIVASTAVA[1]

M. V. Mahavidayalaya, Bhopal, (M. P.)

[Received on 12th January, 1967]

Abstract

Alternative proof of the Neilson's formula for q-Hermite polynomials $H_n(x)$ is given. A generalisation of q-Hermite polynomials is also given along with other results connected with it.

1. Introduction

Carlitz [2, 3] has proved the following identities

$$(1\cdot1)\qquad H_{n+m}(x) = \sum_{r=0}^{min\,(m,\,n)} (-1)^r\, q^{\frac{r}{2}(r-1)} \begin{bmatrix} n \\ r \end{bmatrix} \begin{bmatrix} m \\ r \end{bmatrix} (q)_r,\ H_{m-r}(x)\ H_{n-r}(x).$$

$$(1\cdot2)\qquad U_{n+\nu}(x) = \sum_{r=0}^{n} (-1)^r\, q^{\frac{r}{2}(r-1)} \begin{bmatrix} n \\ r \end{bmatrix} \begin{bmatrix} \nu \\ r \end{bmatrix} (q)_r,\ H_{n-r}(x)\ U_{\nu-r}(x)$$

where

$$(1\cdot3)\qquad H_n(x) = \sum_{r=0}^{n} \begin{bmatrix} n \\ r \end{bmatrix} x^r,$$

$$(1\cdot4)\qquad \begin{bmatrix} n \\ r \end{bmatrix} = \frac{(q)_n}{(q)_r\,(q)_{n-r}},$$

$$(1\cdot5)\qquad (q)_n = (1-q)\,(1-q^2)\,\ldots\,(1-q^n),\ (q)_0 = 1,\ q \neq 0;$$

also

$$(1\cdot6)\qquad \begin{bmatrix} \nu \\ r \end{bmatrix} = \frac{(1-q^\nu)\,(1-q^{\nu-1})\,\ldots\,(1-q^{\nu-r+1})}{(q)_r};$$

ν is not necessarily a positive integer.

In the present note we shall give a different approach of the proof of the above mentioned identities.

Gould-Hopper [4] has defined g_n^r polynomials as

$$(1\cdot7)\qquad g_n^r\,(x, h) = e^{hD^r}\,x^n;\quad D \equiv d/dx\ .$$

1. *Present address*—Department of Mathematics, Bundelkhand College, Jhansi, (U. P.)

These $g_n^r(x, h)$ polynomials are the extension of the Hermite polynomials $H_n(x/2)$. Here we shall define the q-analogoue of $g_n^r(x, h)$ with the help of operational formulae.

2. Carlitz [1] has defined the operator δ as

$$\delta f(x) = \frac{f(x) - f(xq)}{x} \tag{2·1}$$

and $$\delta^r = \delta . \delta^{r-1}$$

The following results are immediate consequence of the operator δ:

$$\delta^r x^n = \begin{cases} \dfrac{(q)_n}{(q)_{n-r}} x^{n-r}; & r \leqslant n \\ 0 \quad ; & r > n, \end{cases} \tag{2·2}$$

$$\delta^n (fx) = x^{-n} q^{-\frac{n}{2}(n-1)} \sum_{r=0}^{n} (-1)^r \begin{bmatrix} n \\ r \end{bmatrix} q^{\frac{(n-r)(n-r-1)}{2}} f(xq^r) \tag{2·3}$$

and

$$f(xq^n) = \sum_{r=0}^{n} (-1)^r \begin{bmatrix} n \\ r \end{bmatrix} q^{\frac{r}{2}(r-1)} x^r \quad \delta^r f(x) \tag{2·4}$$

Carlitz [2] has defined the operator E as

$$Ef(x) = f(xq) \text{ and } E^n f(x) = f(xq^n). \tag{2·6}$$

Thus we see from (2·4) that

$$E^n \equiv \sum_{r=0}^{n} (-1)^r \begin{bmatrix} n \\ r \end{bmatrix} q^{\frac{r}{2}(r-1)} x^r \delta^r \tag{2·7}$$

and from (2·3)

$$\delta^n = x^{-n} q^{-\frac{n(n-1)}{2}} \sum_{r=0}^{n} (-1)^r \begin{bmatrix} n \\ r \end{bmatrix} q^{\frac{(n-r)}{2}(n-r-1)} E^r. \tag{2·8}$$

Now $$\delta^r H_n(x) = \sum_{s=0}^{n} \begin{bmatrix} n \\ s \end{bmatrix} \delta^r x^s$$

$$= \sum_{s=r}^{n} \begin{bmatrix} n \\ s \end{bmatrix} \frac{(q)_s}{(q)_{s-r}} x^{s-r}, \ (r \leqslant n),$$

so that

$$\delta^r H_n(x) = (q)_r \begin{bmatrix} n \\ r \end{bmatrix} H_{n-r}(x) \tag{2·9}$$

Since [2] we have

$$(E + x)^n = \sum_{s=0}^{n} \begin{bmatrix} n \\ s \end{bmatrix} x^{n-s} E^s \tag{2·10}$$

Therefore from (2·6)

$$(E+x)^n = \sum_{s=0}^{n} \begin{bmatrix} n \\ s \end{bmatrix} x^{n-s} \sum_{r=0}^{s} (-1)^r \begin{bmatrix} s \\ r \end{bmatrix} q^{\frac{r}{2}(r-1)} x^r . \delta^r$$

$$= \sum_{r=0}^{n} (-1)^r \begin{bmatrix} n \\ r \end{bmatrix} q^{\frac{r}{2}(r-1)} x^r \sum_{s=r}^{n} \begin{bmatrix} n-r \\ s-r \end{bmatrix} x^{n-s} . \delta^r$$

$$= \sum_{r=0}^{n} (-1)^r \begin{bmatrix} n \\ r \end{bmatrix} q^{\frac{r}{2}(r-1)} x^r \sum_{s=0}^{n-r} \begin{bmatrix} n-r \\ s \end{bmatrix} x^{n-s-r} . \delta^r$$

so that

$$(2\cdot11) \qquad (E+x)^n = \sum_{r=0}^{n} (-1)^r \begin{bmatrix} n \\ r \end{bmatrix} q^{\frac{r}{2}(r-1)} x^r \; H_{n-r}(x) . \delta^r$$

Now we have

$$(E+x)^n \cdot 1 = H_n(x)$$

and hence

$$(2\cdot12) \qquad (E+x)^n H_m(x) = H_{n+m}(x)$$

Thus from (2·11), we have

$$H_{n+m}(x) = \sum_{r=0}^{n} (-1)^r \begin{bmatrix} n \\ r \end{bmatrix} q^{\frac{r}{2}(r-1)} x^r H_{n-r}(x) \delta^r . H_m(x)$$

$$= \sum_{r=0}^{n} (-1)^r \begin{bmatrix} n \\ r \end{bmatrix} q^{\frac{r(r-1)}{2}} x^r H_{n-r}(x) H_{m-r}(x) \begin{bmatrix} m \\ r \end{bmatrix} (q)_r$$

$$= \sum_{r=0}^{n} (-1)^r \begin{bmatrix} n \\ r \end{bmatrix} \begin{bmatrix} m \\ r \end{bmatrix} q^{\frac{r(r-1)}{2}} (q)_r \, x^r H_{n-r}(x) H_{m-r}(x)$$

which is the same as (1·1).

3. Let $U_\nu(x)$ be a function where ν is not necessarily an integer, which satisfies the following recurrence relations :

$$(3\cdot1) \qquad U_{\nu+1}(x) = (1+x) U_\nu(x) - (1-q^\nu) x U_\nu(x)$$

and

$$(3\cdot2) \qquad U_\nu(x) = U_\nu(xq) + (1-q^\nu) x U_{\nu-1}(x).$$

From (3·1) and (3·2) it follows that

$$(3\cdot3) \qquad U_{\nu+1}(x) = x U_\nu(x) + U_\nu(xq).$$

Now we see that

$$(E+x) U_\nu(x) = U_{\nu+1}(x)$$

and

$$(3\cdot4) \qquad (E+x)^n U_\nu(x) = U_{n+\nu}(x).$$

Also

$$(3\cdot5) \qquad \delta U_\nu(x) = (1-q^\nu) U_{\nu-1}(x)$$

and

$$\delta^r U_\nu(x) = \begin{bmatrix} \nu \\ r \end{bmatrix} (q)_r \, U_{\nu-r}(x). \tag{3·6}$$

Hence from (2·11) we have

$$\begin{aligned} U_{n+\nu}(x) &= (E + x)^n \, U_\nu(x) \\ &= \sum_{r=0}^{n} (-1)^r \begin{bmatrix} n \\ r \end{bmatrix} q^{\frac{1}{2}r(r-1)} \, x^r \, H_{n-r}(x) \, \delta^r \, U_\nu(x) \\ &= \sum_{r=0}^{n} (-1)^r \begin{bmatrix} n \\ r \end{bmatrix} \begin{bmatrix} \nu \\ r \end{bmatrix} q^{\frac{1}{2}r(r-1)} \, (q)_r \, x^r \, H_{n-r}(x) \, U_{\nu-r}(x) \end{aligned} \tag{3·7}$$

which is (1·3)

If we now let

$$H_n(x, q^{-1}) = G_n(x, q) = G_n(x),$$
$$U_\nu(x, q^{-1}) = V_\nu(x, q) = V\nu(x)$$

and let $V_\nu(x)$ satisfy the recurrence relations

$$V_{\nu+1}(x) = (1 + x) \, V_\nu(x) + q^{-\nu} \, (1 - q^\nu) \, x \, V_{\nu-1}(x) \tag{3·8}$$

and

$$V_\nu(x) = V_\nu(x\,q) + q^{-\nu}(1 - q^\nu) \, x \, V_{\nu-1}(x). \tag{3·9}$$

Then it is easily proved, on the same lines as for $U_\nu(x)$, that $V_\nu(x)$ satisfies the identity

$$V_{m+\nu}(x) = \sum_{r=0}^{m} q^{r(r-m-\nu)} \begin{bmatrix} m \\ r \end{bmatrix} \begin{bmatrix} \nu \\ r \end{bmatrix} (q)_r \, G_{m-r}(x) \, V_{\nu-r}(x). \tag{3·10}$$

We immediately see that $U_n(x) = H_n(x)$ and $V_n(x) = G_n(x)$ are particular solutions of (3·7) and (3·10) respectively.

4. Carlitz [1] has given

$$e(\delta) \, x^n = H_n(x) \tag{4·1}$$

where

$$e(t) = \prod_{n=0}^{\infty} (1 - q^n \, t)^{-1} = \sum_{n=0}^{\infty} \frac{t^n}{(q)_n},$$

$$\delta \, e(xt) = t \, e(xt) \tag{4·2}$$

and

$$e(\delta) \, e(xt) = e(t) \, e(xt). \tag{4·3}$$

Hence

$$e(\delta)\, e(xt) = \sum_{n=0}^{\infty} \frac{H_n(x)}{(q)_n} t^n. \tag{4·4}$$

Let us define the function $H_n^r(x, h)$ as

$$e(h\,\delta^r)\, x^n = H_n^r(x, h). \tag{4·5}$$

Now we see that

$$e(h\,\delta^r)\, x^n = \sum_{k=0}^{[n/r]} \frac{(q)_n\, x^{n-kr}}{(q)_k\, (q)_{n-kr}} h^k \tag{4·6}$$

where $[\, n/r\,]$ is the greatest integer in (n/r).

Thus

$$H_n^r(x, h) = \sum_{k=0}^{[n/r]} \frac{(q)_n\, x^{n-kr}}{(q)_k\, (q)_{n-kr}} h^k. \tag{4·7}$$

We immediately see that $H_n^r(x, h)$ is q-analogoue of $g_n^r(x, h)$ of [4].

It is easily proved that

$$e(h\,\delta^r)\, e(xt) = e(ht^r)\, e(xt). \tag{4·8}$$

Hence the generating function of $H_n^r(x, h)$ is given by

$$e(ht^r)\, e(xt) = \sum_{n=0}^{\infty} H_n^r(x, h) \frac{t^n}{(q)_n}. \tag{4·9}$$

Further we see that

$$\delta\, H_n^r(x, h) = (1 - q^n)\, H^r_{n-1}(x, h) \tag{4·10}$$

and

$$\delta^j H_n^r(x, h) = (q)_j \begin{bmatrix} n \\ j \end{bmatrix} H^r_{n-j}(x, h). \tag{4·11}$$

Again, we get here one of the interesting result as

$$e(h\,\delta^r)\, [x^n\, e(xt)] = \delta_t^n\, [e(ht^r)\, e(xt)] \tag{4·12}$$

where δ_t denotes the operation with respect to t.

To prove (4·12) we have

$$\delta_t\, [e(ht^r)\, e(xt)] = \sum_{n=0}^{\infty} H^r{}_{n+1}(x, h) \frac{t^n}{(q)_n}, \tag{4·13}$$

and hence

$$\delta_t{}^m\, [e(ht^r)\, e(xt)] = \sum_{n=0}^{\infty} H^r{}_{n+m}(x, n) \frac{t^n}{(q)_n}. \tag{4·14}$$

Also

$$e(h\,\delta^r)\,[x^m\,e(xt)]$$

$$= e(h\,\delta^r) \sum_{s=0}^{\infty} \frac{x^{m+s}}{(q)_s}\, t^s$$

$$= \sum_{n=0}^{\infty} \sum_{s=0}^{\infty} \frac{h^n\,\delta^{rn}\,x^{m+s}}{(q)_n\,(q)_s}\, t^s$$

$$= \sum_{s=0}^{\infty} \frac{t^s}{(q)_s} \left[\frac{m+s}{r}\right]! \sum_{n=0} \frac{h^n (q)_{m+s}\, x^{m+s-rn}}{(q)_n\,(q)_{m+s-rn}}$$

$$= \sum_{s=0}^{\infty} \frac{t^s}{(q)_s}\, H^r{}_{m+s}(x, h).$$

Thus the proof of (4·12) is complete.

If $f(x)$ is a power series, then from (4·12), we have

(4·15) $$e(h\delta^r)\,[f(x)\,e(tx)] = f(\delta_t)\,[e(ht^r)\,e(tx)].$$

As a special case, let us take

$$f(x) = e(j\,x^r)$$

then

(4·16) $$e(h\,\delta^r)\,[e(jx^r)\,e(t\,x)] = e\left(j\delta_t^{\,r}\right)[e(ht^r)\,e(tx)].$$

We see that the formula (4·16) is a symmetric with respect to t and x.

Recurrence relations for $H_n^r(x, h)$ are complicated and are not easily derivable.

Acknowledgement

I am indebted to Dr. R. P. Singh for the guidance during the preparation of this note.

References

1. Carlitz, L. A q-identity, *Monatshefte Für Mathematic Sonderabdnick*, aus 67, Band 63, 4 Heftder, 305-310.
2. ——— Some polynomials related to Theta Functions. *Duke Math. Jour.*, **57** : 521–526.
3. ——— Some polynomials related to Theta functions. *Annuli Di Mathematica. Serie IV Toma*, **41** : 359–373, 1955.
4. Gould, H. W. and Hopper, A. T. Operational formulas connected with two generalisations of Hermite polynomials. *Duke Math. Jour.*, **29** (1): 51–64, 1962.

Proc. Nat Acad. Sci., India, 38(A), I & II, 1968

Solution of a pair of Dual integral equations

By

S. L. KALLA

Department of Mathematics, M. R. Engineering College, Jaipur

[Received on 10th January, 1967]

Abstract

A formal solution of the dual integral equations,

$$\int_0^\infty t^\alpha J_\mu(xt)\, g(t)\, dt = f(x), \qquad 0 < x < 1.$$

$$\int_0^\infty t\beta J_\nu(xt)\, g(t)\, dt = F(x), \qquad x > 1.$$

is derived in this paper.

1. Introduction

When the theory of Hankel transforms is applied to the solution ol certain mixed boundary value problems in Mathematical Physics, the problems are reduced to the solution of dual integral equations of the type.

$$\int_0^\infty t^\alpha J_\mu(xt)\, g(t)\, dt = f(x), \qquad 0 < x < 1 \tag{1·1}$$

$$\int_0^\infty t\beta J_\nu(xt)\, g(t)\, dt = F(x), \qquad x > 1 \tag{1·2}$$

Where α, β, μ, ν are prescribed constants and $f(x)$, $F(x)$ are prescribed functions of x and $g(t)$ is to be determined.

Equations of this type were first given by Weber [15], who obtained the solution for the case in which $\alpha = -1$, $\beta = \mu = \nu = 0$, $f \equiv 1$ and $F \equiv 0$. Various solutions of dual integral equations which can be formed from (1·1) and (1·2) have been given by many authors. The first direct solution of a pair of equations of this type was given by Beltrami [1]. The formal solution for the case $\beta = 0$, $\mu = \nu$ and $F(x) \equiv 0$ was first derived by Titchmarsh [11] by using Weiner-Hopf procedure. Noble [8] has also obtained the solution of a general case of above type. Noble's method is an extension of that doveloped by Copson [3], for the problem of electrified disc. Busbridge [2] and Gordon [7] have also considered similar pair of dual integral equations. Williams [17] has also given a solution for the case $\beta = 0$, $\mu = \nu$ by a formal application of the theory of Mellin transforms. A solution of the pair of equations (1·1) and (1·2) in the case $\alpha = \pm 1$, $\beta = 0$, $\mu = \nu$ was given by Tranter [12]. Srivastava [10] has also considered a pair for the case $\beta = 0$ and $\mu = \nu$. Recently Rathie [9] has also considered a pair of equations and generalise the solution earlier given by Tranter [12].

Recently few authors have used certain operators introduced in the theory of fractional integration for solving dual integral equations of the type (1·1) and (1·2). Erdelyi and Sneddon [5] have obtained a solution of the similar pair by means of fractional operators. Fox [6] has also given the solution of dual integral equations involving generalized kernels.

The object of the present paper is to obtain a solution of integral equations (1·1) and (1·2) by using Sonine's generalized first integral due to Tranter [13] and Abel's integral equation [16, p. 229].

2. We shall need the following results in deriving the solution of the dual integral equations (1·1) and (1·2).

(*i*) The following well known result in the theory of Bessel functions [14, p. 401].

$$\int_0^\infty x^{\mu-\lambda+1} J_\lambda(ax) J_\mu(bx)\, dx = 0 \quad , \quad 0 < a < b$$

$$= \frac{b^\mu (a^2 - b^2)^{\lambda-\mu-1}}{2^{\lambda-\mu-1} a^\lambda \Gamma(\lambda-\mu)} \quad , \quad 0 < b < a. \qquad (2{\cdot}1)$$

(*ii*) the generalization of Sonine's first integral as given by Tranter [13, p. 97].

$$\int_0^{\pi/2} \mathrm{Sin}^{\nu+1}\theta \cos^{2\mu+1}\theta\, J_\nu(2\sin\theta)\, {}_2F_1(-n, \mu+\nu+n+1 ; \nu+1 ; \sin^2\theta)\, d\theta$$

$$= \frac{2^\mu \Gamma(\nu+1)\Gamma(\mu+n+1)}{z^{\mu+1}\Gamma(\nu+n+1)} J_{\mu+\nu+2n+1}(z), \qquad (2{\cdot}2)$$

for $R(\mu+1) > 0$, $R(\nu+1) > 0$, $n = 0, 1, 2, \ldots$.

(*iii*) the following result [4, p. 333]

$$\int_0^a x^{\nu+1} J_\nu(x)\, dx = a^{\nu+1} J_{\nu+1}(a), \qquad (2{\cdot}3)$$

for $R(\nu+1) > 0$.

(*iv*) the solution of Abel's integral equation, [16, p. 229].

$$f(x^2) = 2\int_0^x \frac{t\, g(t^2)\, dt}{(x^2-t^2)^\mu}, \qquad (2{\cdot}4)$$

in the form

$$g(x) = \frac{\sin\mu\pi}{\pi} \frac{d}{dx}\int_0^x \frac{f(t)\, dt}{(x-t)^{1-\mu}} \qquad (2{\cdot}5)$$

where $f'(x)$ is continuous, $f(0) = 0$, $0 < \mu < 1$, $0 \leq x \leq b$.

3. Solution of integral equations (1·1) and (1·2)

Applying the Hankel inversion theorem to equation (1·2),

$$t^{\beta-1} g(t) = \int_0^1 x\, V(x)\, J_\nu(xt)\, dx + \int_1^\infty x\, F(x)\, J_\nu(xt)\, dx \qquad (3{\cdot}1)$$

where

$$V(x) = \int_0^\infty t^\beta J_\nu(xt)\, g(t)\, dt \quad , \quad 0 < x < 1$$

let

$$V(x) = x^{\nu}\left\{F(1) + \frac{\pi^{\frac{1}{2}}\,\Gamma(\nu+n+1)\,2^{\frac{1}{2}(\beta+\nu+2n-\mu-\alpha+1)}}{\Gamma(\nu+1)\,\Gamma\{\frac{1}{2}(\mu+\alpha-\beta-\nu)\}} \times \right.$$

$$\left.\int_x^1 \chi(\zeta)\,(\zeta^2-x^2)^{\frac{1}{2}(\mu+\alpha-\beta-\nu-2n-2)}\,{}_2F_1\left(\begin{matrix}-n,\ \frac{1}{2}(\mu+\alpha-\beta+\nu)\\ \nu+1\end{matrix};\ \frac{x^2}{\zeta^2}\right) ds\right\} \quad (3\cdot2)$$

Hence

$$\int_0^1 x\,V(x)\,J_{\nu}(xt)\,dx$$

$$= F(1)\int_0^1 x^{\nu+1}J_{\nu}(xt)\,dx + \frac{\pi^{\frac{1}{2}}\,\Gamma(\nu+n+1)\,2^{\frac{1}{2}(\beta+\nu+2n-\mu-\alpha+1)}}{\Gamma(\nu+1)\,\Gamma\{\frac{1}{2}(\mu+\alpha-\beta-\nu)\}} \times$$

$$\int_0^1 x^{\nu+1}J_{\nu}(xt)\left[\int_x^1 \chi(\zeta)\,(\zeta^2-x^2)^{\frac{1}{2}(\mu+\alpha-\beta-\nu-2n-1)}\,{}_2F_1\left(\begin{matrix}-n,\frac{1}{2}(\mu+\alpha-\beta+\nu)\\ \nu+1\end{matrix};\frac{x^2}{\zeta^2}\right)ds\right]dx$$

On using (2·3) and interchanging the order of integration we get,

$$= F(1)\,t^{-1}J_{\nu+1}(t) + \frac{\pi^{\frac{1}{2}}\,\Gamma(\nu+n+1)\,2^{\frac{1}{2}(\beta+\nu+2n-\mu-\alpha+1)}}{\Gamma(\nu+1)\,\Gamma\{\frac{1}{2}(\mu+\alpha-\beta-\nu)\}}\int_0^1 \chi(\zeta)$$

$$\left[\int_0^{\zeta} x^{\nu+1}\,(\zeta^2-x^2)^{\frac{1}{2}(\mu+\alpha-\beta-\nu-2n-2)}\,J_{\nu}(xt)\,{}_2F_1\left(\begin{matrix}-n,\ \frac{1}{2}(\mu+\alpha-\beta+\nu)\\ \nu+1\end{matrix};\ \frac{x^2}{\zeta^2}\right)dx\right]ds$$

then using (2·2) we obtain,

$$= F(1)\,t^{-1}J_{\nu+1}(t) + \left(\frac{\pi}{2}\right)^{\frac{1}{2}} t^{-\frac{1}{2}(\mu+\alpha-\beta-\nu-2n)} \times$$

$$\int_0^1 \zeta^{\frac{1}{2}(\mu+\alpha-\beta+\nu-2n)}\,J_{\frac{1}{2}(\mu+\alpha-\beta+\nu+2n)}(\zeta t)\,\chi(\zeta)\,ds.$$

Therefore

$$g(t) = H(t) + \left(\frac{\pi}{2}\right)^{\frac{1}{2}} t^{-\frac{1}{2}(\mu+\alpha+\beta-\nu-2n-2)} \times \quad (3\cdot3)$$

$$\int_0^1 \zeta^{\frac{1}{2}(\mu+\alpha-\beta-\nu-2n)}\,J_{\frac{1}{2}(\mu+\alpha-\beta+\nu+2n)}(st)\,\chi(\zeta)\,ds$$

where,

$$H(t) = F(1)\,t^{1-\beta}J_{\nu+1}(t) + t^{1-\beta}\int_1^{\infty} x\,F(x)\,J_{\nu}(xt)\,dx. \quad (3\cdot4)$$

On multiplying (1·1) by $x^{\mu+1}$ and integrating with respect to x from 0 to x, we get the following expression on interchanging the order of integration and evaluation the x-integral by (2·3)

$$\int_0^{\infty} t^{\alpha-1}J_{\mu+1}(xt)\,g(t)\,dt = x^{-\mu-1}\int_0^x x^{\mu+1}f(x)\,dx, \quad 0 < x < 1.$$

Putting the value of $g(t)$ from (3·3) in the above expression, we obtain,

$$\int_0^{\infty} t^{-\frac{1}{2}(\mu-\alpha+\beta-\nu-2n)}J_{\mu+1}(xt)\,dt \int_0^1 \zeta^{\frac{1}{2}(\mu+\alpha-\beta+\nu-2n)}J_{\frac{1}{2}(\mu+\alpha-\beta+\nu+2n)}(st)\,\chi(s)\,ds,$$

$$= P(x)$$

where

$$\sqrt{\frac{\pi}{2}}\,P(x) = x^{-\mu-1}\int_0^x x^{\mu+1}f(x)\,dx - \int_0^{\infty} t^{\alpha-1}H(t)\,J_{\mu+1}(xt)\,dt. \quad (3\cdot5)$$

How on interchanging the order of integration and evaluating the t-integral by (2·1), we get,

$$2\int_0^x S^{\mu+\alpha-\beta+\nu}\,(x^2-\zeta^2)^{-\frac{1}{2}(\alpha-\mu-\beta+\nu+2n)}\,\chi(\zeta)\,ds$$

$$= 2^{\frac{1}{2}(\mu+\beta-\nu-\alpha-2n+2)}\,\Gamma\{\tfrac{1}{2}(\mu+\beta-\alpha-\nu-2n+2)\}\,x^{\mu+1}P(x) \quad (3\cdot6)$$

then using (2·5) we get,

$$S^{\frac{1}{2}(\mu+\alpha-\beta+\nu-1)}\,\chi(\sqrt{s}) = 2^{\frac{1}{2}(\mu+\beta-\nu-\alpha-2n+2)}\,\Gamma\{\tfrac{1}{2}(\mu+\beta-\alpha-\nu-2n+2)\}\,\pi^{-1}\times$$

$$\text{Sin}\,(\alpha-\mu-\beta+\nu+2n)\,\frac{\pi}{2}\,\frac{d}{dx}\int_0^x \frac{t^{\frac{1}{2}(\mu+1)}\,P(\sqrt{t})\,dt}{(x-t)^{\frac{1}{2}(2-\alpha+\mu+\beta-\nu-2n)}} \qquad (3\cdot7)$$

Hence the solution of the integral equations (1·1) and (1·2) is given by (3·3), $H(t)$ is given by (3·4) and $P(x)$ and $\chi(\zeta)$ by (3·5 and (3·7) respectively.

The solution given above is purely formal and following assumptions have been made.

(*i*) $R(\nu+1)>0$, $R(\mu+1)>0$ $n=0, 1, 2\ldots.$

(*ii*) Certain integrals which occur in the course of analysis exist and the order of integration in certain integrals can be interchanged.

(*iii*) $P'(x)$ is continuous, $P(0)=0$ and $0<\alpha-\mu-\beta+\nu+2n<2$.

Acknowledgements

The author is highly grateful to Dr. P. N. Rathie of M. R. Engineering College, Jaipur for his keen interest during the preparation of this paper. Author's sincere thanks are also due to the Ministry of Education, Govt. of India, for awarding research training Scholarship.

References

1. Beltrami, E. Sulla teoria della funzioni potenziali simmetriche. *Rend. Acad. Sci. di Bologna*, 461, 1881.
2. Busbridge, I. W. Dual integral equations. *Proc. London Math. Soc*, **44**: 115, 1938.
3. Copson, E. T. On certain dual integral equations. *Proc. Glasgow Math. Asso.*, **5**: 21, 1961.
4. Erdelyi, A. *et al.* Tables of integral transforms **Vol. II**: *McGraw-Hill, New York*, 1954.
5. Erdelyi, A. and Sneddon, I. N. Fractional integration and dual integral equation, *Can. J. Math.*, **14**: 685, 1962.
6. Fox. C. A formal solution of certain dual integral equations. *Trans. Amer. Math. Soc.*, **119**: 389–398, 1965.
7. Gordon, A. N. Dual integral equations. *J. London Math. Soc.*, **29**: 360–363, 1954.
8. Noble, B. On some dual integral equations. *Quart. J. Math.*, **6** (2): 81, 1955.
9. Rathie, P. N. A pair of dual integral equations, occurring in boundary value problems I and II, communicated for publication, 1966.
10. Srivastava, K. N. On certain dual integral equations. *J. Indian Math. Soc.*, **29**: 81–86, 1965.
11. Titchmarsh, E. C. Introduction to the theory of Fourier integrals. *Oxford*, 334, 1937.
12. Tranter, C. J. On some dual integral equations. *Quart. J. Math.* 2 (2): 60-66, 1951.
13. Tranter, C. J. A generalization of Sonine's first finite integral. *Proc. Glasgow. Math. Assc.*, **6**: 97-98, 1963.
14. Watson, G. N. A treatise on the theory of Bessel functions. *Cambridge*, 1944.
15. Webber, H. Über die Besselchen Funktionen und ihre Anwendung on die Theorie der Elektrischen Strome. *J. F. Math.*, **75**: 75, 1873.
16. Whittaker, E. T. and Watson, G. N. A course of modern analysis. *Cambridge*, 1963.
17. Williams, W. E. The solution of certain dual integral equations. *Proc. Edinburgh Math. Soc.*, **12**: 213, 1961.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968

Nitrification Studies in Black Soil

By

S. P. TANDON & M. M. MISHRA

Department of Chemistry, University of Allahabad

[Received on 12th January, 1967]

Introduction

The growth and activity of nitrifying bacteria primarily depend on the chemical, physical and biological properties of the soil where they occur. Chemical composition of soil varies from place to place, and hence the extent of the growth of the micro-organism may also differ from place to place.

In order to study the growth of the nitrate-forming bacterium in the medium containing soil alone, and soil along with carbonates of Ca, Mg and Na, we have carried out extensive experiments. The soil taken was black soil, the chemical composition of which, as found by Dr. S. C. Mishra and his coworkers, is given below :

Silica	73·680%
Sesquioxide	17·470%
Calcium oxide	1·204%
Manganese	0·090%
Phosphoric acid (P_2O_5)	0·09625%
Organic carbon	0·57%
Total nitrogen	0·087%
Ammonical nitrogen	0·0035%
Nitrite nitrogen	0·000345%
Nitrate nitrogen	0·0056%
Water soluble-chloride	0·00816%
Water soluble-sulphate	0·00501%
Cation exchange capacity (m.e./100 gm)	36·4

Experimental

The following solutions were taken :

Solution A—sterilized sodium nitrite solution containing one mg nitrogen per ml.

Solution B—containing all the constituents of Fred and Davenport's[1] medium except sodium nitrite.

For the systematic study, six sets, each comprising of four 250 ml conical flasks were taken. In each flask of the first two sets 1·0 g, in each flask of the next two sets 2 g, and in each flask of the last 2 sets 3 g of the soil were taken. In this way the above six sets were split up into three groups, each group comprising of two sets. Into each of the three flasks of every set 0·01, 0·05 and 0·10 g of $MgCO_3$ was added. The fourth flask of each set was left as such with no carbonate. 50 ml distilled water was then added to the contents of each flask. One more flask with 50 ml of the solution-B was also taken. 0·2 ml of the solution-A was then added to each of the above flasks. All the flasks were

sterilized at 15 lbs pressure for 15 minutes in an electric autoclave. After sterilization the flasks were allowed to cool and then 1 ml inoculum of a pure culture of *Nitrobacter agilis* was introduced into each of the flasks, and all the flasks were kept in an incubator.

The rate of nitrite oxidation by the bacterium was taken to relate to its growth and activity.

Nitrite was estimated in all the flasks of one set of each group after 48, 96, 168, 240 and 360 hrs by Griess-Ilosovay method[2].

Total nitrogen (nitrite + nitrate) was estimated in the flasks of the other set of each group in the beginning and at the end of each experiment by Brucine method[3].

TABLE 1

Nitrite oxidation in the presence of black soil in the medium

Nature of medium	Nitrite nitrogen left at different intervals of time (in mg) Time in hours				
	48	96	168	240	360
Fred and Davenport's medium.	0·1561	0·0701	0·0038	–	–
1·0 g soil + 50 ml distilled water.	0·1633	0·0853	0·0138	–	–
2·0 g soil + 50 ml distilled water.	0·1669	0·1107	0·0428	–	–
3·0 g soil + 50 ml distilled water.	0·1742	0·1252	0·0609	–	–

TABLE 2

Nitrite oxidation in soil suspension in presence of $CaCO_3$

Amount of soil present per 50 ml (in gm)	Amount of $CaCO_3$ taken (in gm)	Nitrite nitrogen left after 96 hours (in mg)
Fred and Davenport's liquid medium	–	0·0701
1 gm + 50 ml distilled water	–	0·0853
1 gm + ,, ,,	0·01	0·0744
1 gm + ,, ,,	0·05	0·0599
1 gm + ,, ,,	0·10	0·0701
2 gm + ,, ,,	–	0·1107
2 gm + ,, ,,	0·01	0·1035
2 gm + ,, ,,	0·05	0·0780
2 gm + ,, ,,	0·10	0·0853
3 gm + ,, ,,	–	0·1252
3 gm + ,, ,,	0·01	0·1107
3 gm + ,, ,,	0·05	0·0853
3 gm + ,, ,,	0·10	0·0610

TABLE 3

Nitrite oxidation in soil suspension in presence of $MgCO_3$

Amount of soil present per 50 ml (in gm)	Amount of $MgCO_3$ taken per 50 ml (in gm)	Nitrite nitrogen left after 96 hours (in mg)
Fred and Davenport's liquid medium	–	0·0701
1 gm + 50 ml distilled water	–	0·0853
1 gm + ,, ,,	0·01	0·0701
1 gm + ,, ,,	0.05	0·0889
1 gm + ,, ,,	0·10	0·1031
2 gm + ,, ,,	–	0·1107
2 gm + ,, ,	0·01	0·0889
2 gm + ,, ,,	0·05	0·0962
2 gm + ,, ,,	0·10	0·1107
3 gm + ,, ,,	–	0·1252
3 gm + ,, ,,	0·01	0·1107
3 gm + ,, ,,	0·05	0·1034
3 gm + ,, ,,	0·10	0·0951

TABLE 4

Nitrite oxidation in soil suspension in presence of Na_2CO_3

Amount of soil present per 50 ml (in gm)	Amount of sodium carbonate taken (in gm)	Nitrite nitrogen left after 96 hours (in mg)
Fred and Davenport's liquid medium	–	0·0701
1 gm + 50 ml distilled water	–	0·0853
1 gm + ,, ,,	0·01	0·0889
1 gm + ,, ,,	0·05	0·1206
1 gm + ,, ,,	0·10	0·1287
2 gm + ,, ,,	–	0·1107
2 gm + ,, ,,	0·01	0·1198
2 gm + ,, ,,	0·05	0·1252
2 gm + ,, ,,	0·10	0·1307
3 gm + ,, ,,	–	0·1252
3 gm + ,, ,,	0·01	0·1206
3 gm + ,, ,,	0·05	0·1336
3 gm + ,, ,,	0·10	0·1416

Results and Discussion*

The results obtained indicate that when the black soil alone is used as a medium of growth for *Nitrobacter agilis* the nitrite oxidation is fairly satisfactory, but it is comparatively less than when Fred and Davenport's medium is used

*The original nitrite content of the soil was subtracted from the nitrite left after oxidation in all those experiments in which soil was employed so that the data could become comparable to those obtained with Fred and Davenport's liquid culture medium.

Total nitrogen (nitrite + nitrate) remains the same at the end of each experiment which clearly indicates that nitrite which disappears, gets changed only to nitrate.

(Table 1). Maximum nitrate formation takes place when only 1·0 g black soil is present in 50 ml of the medium. But as the amount the black soil in the medium increases, the rate of nitrite oxidation decreases though at a very slow rate.

It is also observed that the addition of $CaCO_3$ along with the black soil further enhances the rate of nitrification (Table 2). Amongst the various ratios of soil and $CaCO_3$ present in the individual suspension, the suspension having 1·0 g of the soil with $0·0^5$ g of $CaCO_3$ produces maximum nitrification. Only 0·0599 mg nitrogen in the form of nitrite was left in this solution after 96 hours of incubation, whereas in the Fred and Davenport's medium after the same period the amount of nitrite nitrogen left was 0·0701 mg. This may be because $CaCO_3$ helps in making available the reserve nutrient meterial of all kinds to the bacterium in the soil. It also exerts a very beneficial action by neutralising the acids produced during nitrification and thus maintaining a proper reaction.

The formation of nitrate from nitrite by *Nitrobacter agilis* in a medium containing the soil along with $MgCO_3$ is also fairly good (Table 3). It is more than what occurs when the soil alone is taken. This may be due to the fact that in the presence of $MgCO_3$, the pH of the solution becomes slightly alkaline and consequently the metabolic processes of the organism are expected to be stimulated. (Magnesium plays an essential role in many enzymatic reactions, particularly in phosphorylating reaction[4]). Maximum nitrite oxidation takes place in the medium containing 1·0 g of the black soil along with 0·01 g of $MgCO_3$. The amount of nitrogen left in the form of nitrite in this medium after 96 hours was 0·0701 mg, whereas in the medium containing only, 1·0 g of the soil but no carbonate, the amount of nitrite nitrogen left after the same period was 0·0853 mg.

The presence of Na_2CO_3 in the medium along with the soil results in decrease in the rate of nitrification (Table 4). In our earlier studies (unpublished) we have found that when talc is used as a medium of growth, the presence of sodium carbonate accelerates the rate of nitrate formation. The harmful effect of Na_2CO_3 when present along with the soil may be due to the fact that the saline solution dissolves some of the humus present in the soil and also causes resolution of the clay material into its finest particles. Clay becomes sodium saturated and hence defloccùlated.

Summary

Studies were made on nitrification by the nitrate-forming bacterium *Nitrobacter agilis*, in the medium containing black soil alone and the soil along with carbonates of Ca, Mg and Na. It was found that in the presence of soil alone, the rate of oxidation of nitrite to nitrate by the bacterium is fairiy satisfactory, although not so good as in the Fred and Davenport's medium. The presence of $CaCO_3$ along with the soil enhances the rate of nitrification considerably, the presence of $MgCO_3$ along with the soil also increases the rate of nitrate-formation to some extent, but the presence of Na_2CO_3 along with the soil slows down the process.

References

1. Fred, E. B. and Waksman, S. "Laboratory manual of gen. Microbiol. with special reference to the Micro-organisms of the Soil" Ed. 1928.
2. Meiklejohn, J. *J. Gen. Microbiol.*, **4** : 185, 1950.
3. Boltz, D. F. (Editor). "Colorimeteric determination of non-metal." 141-44, Ed., 1958.
4. Bomecke, H. *Arch. Microbiol.*, **14** : 63, 1949.

Proc Nat. Acad. Sci India, 38(A), I & II, 1968

Mechanism of the Catalytic Activity of Silver Ions in Peroxydisulphate Oxidations

By

D. D. MISHRA

Department of Post-graduate Studies and Research in Chemistry, University of Jabalpur, Jabalpur (M. P.) India

[Received on 28th January, 1967]

Abstract

The catalytic activity of silver ions, for several oxidations, studied with peroxydisulphate, has been ascribed to the formation of an intermediate higher-valent silver. The nature of these highervalent species and also the reaction between $S_2O_8^{-2}$ and Ag^+ to yield these forms is still obsecure. In several communications on oxidations of inorgani c compounds by this oxidising agent D. M. Yost has suggested the rate determining step to be the interaction of $S_2O_8^{-2}$ and Ag^+ ions because of the lack of dependence of the rate law in reductant concentration. In our earlier publications[1] it has been reported that the rate determining step in the oxidations of some of the organic compounds is the interaction of highervalent silver with the reducing substrate. Potassium flouride complexes with Ag^{+3} and Pyridine with Ag^{+2} and the presence of potassium flouride with the interaction solutions considerably delays the precipitation and the residue obtained after 40 minutes has the formula $Ag_2O_{2\cdot2}$. It is suggested that Ag^{+3} is the chief reactive specy in the catalysed oxidations of glycerol and glycol whilst it is Ag^{+2} for ethanol and dioxane oxidations.

Introduction

Bivalent and trivalent silver as unstable intermediate have been postulated to explain the catalytic activity of silver (I). The nature of these active species (bivalent and trivalent) is still obscure and this has been here.

The study of the properties of highervalent silver has been made by Noyes[2] Palagyi[3] *et al* and very recently by Sutcliffe[4] *et al*. These highervalent species were prepared by these workers by ozonolysis of silver (1) compound in nitric acid or perchloric acid. I have, however, prepared these compounds for our study by the interaction of peroxydisulphate and silver nitrate of suitable concentrations.

Experimental

The chemicals used were all of A.R. quality. Potassium peroxydisulphate solution was freshly prepared. The concentrations of $K_2S_2O_8$ and $AgNO_3$ chosen for the experiments to produce the residue (containing higervalent silver oxide) were in no case less than 0·1 M. The black residue thus formed was centrifuged and quickly washed with bidistilled water till the filtrate was free from peroxydisulphate and sulphate, which hardly took 5 to 6 minutes. The composition of the black residue was determined by measuring its oxidative capacity by two methods.

In one of the methods, two samples of the black residues were prepared under identical conditions. One of the residues was treated with acidified potassium iodide and the liberated iodine was titrated with standardised hypo solution. The other residue was treated with nitric acid when it evolved oxygen rapidly and passed into solution, which when treated with dilute hydrochloric acid gave precipitate of silver chloride, which was estimated in a cintered glass crucible.

The other method was followed by adding an excess of a known volume of acidified ferrous salt solution and the excess left over was titrated with a standard solution of permanganate. This solution left after the titration was used to determine the silver content by titrating it with a standard thiocynate solution, the ferric salt present therein acted as an indicator.

Results and Discussion

Table 1 gives the formula of the black residue calculated from the results for its oxidative capacity and silver content. These values are the mean of the results of three or more experiments, which differ within 2%.

TABLE 1

Formula of the black residue obtained after the interaction of different concentration of the reactants for a specified time

Concentration of the reactants in Molarity	Time of interaction in minutes	Formula of the precipitate
0·1	30	$Ag_2O_{2\cdot23}$
0·025	30	$Ag_2O_{2\cdot15}$
0·0125	30	Ag_2O_2
0·00625	30	Very slight turbidity.

The table below gives the formula of the black residue obtained by the interaction of the solutions of silver nitrate and potassium peroxydisulphate (each 0·1M concentration) for different lengths of time.

TABLE 2

Time in minutes	Medium (initial)	Formula of the precipitate
8	Neutral	$Ag_2O_{2\cdot28}$
8	Slightly alkaline	$Ag_2O_{2\cdot50}$
16	Neutral	$Ag_2O_{2\cdot56}$
30	Neutral	$Ag_2O_{2\cdot28}$
40	Neutral	$Ag_2O_{2\cdot06}$

It will be seen from the table 2 that the amount of oxygen associated with the precipitate is in all cases more than that required for the bivalent silver viz. Ag_2O_2. The excess of oxygen associated with the precipitate may thus be ascribed to the formation of higher oxide Ag_2O_3.

Table 3 gives the proportions of Ag_2O_3 and Ag_2O_2 in the different samples.

TABLE 3

Time in minutes	Amount of Ag_2O_3	Amount of Ag_2O_2
8	0·28	0·72
16	0·56	0·44
30	0·28	0·72
40	0·06	0·94

Therefore, it appears that trivalent silver Ag_2O_3 is unstable and tends to decompose to lower oxides of silver.

Trivalent silver is known to form a complex with potassium fluoride while Ag^{+2} forms a complex with pyridine[5]. It is found that when potassium flouride is present with the interacting solution the precipitation is considerably delayed and the residue obtained has the formula $Ag_2O_{2\cdot2}$. But in the case of pyridine a black residue immediately appeared which dissolved in the solution but on keeping for a long time yielded a precipitate of metallic silver. The observation, therefore, indicates that Ag_2O_3, it immediately formed by the interaction of silver nitrate and potassium peroxydisulphate, which decomposes yielding the stabler product bivalent silver oxide. This conclusion appears to be not in consonance with my results given in table 2 where within 8 minutes of the interaction of 0·1M $K_2S_2O_8$ with 0·1M $AgNO_3$ produces the residue in neutral medium of formula $Ag_2O_{2\cdot28}$ containing only 28% of Ag_2O_3, which increases to 56% in 16 minutes. This result is expected if, when the reaction between Ag^{+3} and Ag^{+1} remaining unreacted form Ag^{+2} according to :

$$Ag^{+3} + Ag^{+1} \underset{K_1}{\overset{K_2}{\rightleftharpoons}} 2Ag^{+2}$$

K_2 the rate constant is very large. Indeed, I have found that the black residue resulting by the interaction of 0·01M potassium peroxydisulphate and 0·05M silver nitrate did not produce at any stage any higher oxide of silver greater than bivalent one. It should be clearly stated here that the loss of Ag^{+3} arises out of the forward reaction in the above equilibria and also by the direct interaction of Ag^{+3} with water. Hence the amount of trivalent silver formed first increases to a maximum value which gradually tends to yield Ag_2O_2 as has been noted under tables 2 and 3.

In recent communication Sutcliffe (loc. cit.) opines that the decomposition of Ag^{+3} is a slow process. My results do not contribute to this conclusion and they distinctly show that in the solid residue of a mixture of Ag^{+3} and Ag^{+2} (also of palagyi) the decomposition of Ag^{+3} is fast whilst Ag^{+2} is comparatively stable. Moreover, I have been able to show that the first product of the oxidation of Ag^{+} ions by peroxydisulphate is Ag^{+3}. I therefore suggest that :

$$-\frac{d(Ag^{+2})}{dt} \propto \frac{(Ag^{+2})^2}{Ag^{+1}}$$

will equally hold good if we assure that K_2 is very large compared to K_1 and that K is rapid. The catalytic influence may be due to both these higher oxides and it has been repeatedly found in all the experiments that the rate constants in the initial stage is always different (in most cases very higher than the subsequent rate constants). In the following tables the first order rate constants calculated with the progress of the reaction are noted to show this fact.

TABLE 4

$(K_2S_2O_8)$ = 0·02 M Temperature = 30°C

Glycerol 0·8 M $AgNO_3$ 0·001 M values of rate constants $K/2·303 \times 10^4$	Glycerol 0·8 M $AgNO_3$ 0·002 M values of rate constants $K/2·303 \times 10^4$	Glycerol 0·8 M $AgNO_3$ 0·004 M values of rate constants $K/2·303 \times 10^4$
15·37	25·93	64·30
11·31	22·60	37·50
10·12	18·61	34·60
9·04	16·84	33·05
9·15	15·97	32·24
8·76	15·41	31·74
8·59	–	30·68
8·46	15·28	30·60
8·45	15·22	30·37
8·43	14·63	29·59

These results definitely show that the first drop in the values of the rate constants is due to the rapid decomposition of Ag^{+3} by means of the two reactions (2) and (3) and the production of the same is due to the interaction of peroxydisulphate and silver nitrate shows in the equation (1).

$$S_2O_8^{-2} + Ag^{+1} \rightarrow Ag^{+3} + 2SO_4^{-2} \quad (1)$$

$$2Ag^{+2} + \rightleftharpoons Ag^{+3} + Ag^{+1} \quad (2)$$

$$Ag^{+3} + H_2O \rightarrow Ag^{+2} + H^+ + OH \quad (3)$$

As soon as Ag^{+2} is formed in the sufficient quantity its decomposition attains a steady rate with the result in the latter stages of the above reactions the values of the rate constants are in better agreement. Further Ag^{+2} decomposes in the manner given below :

$$Ag^{+2} + H_2O \rightarrow Ag^{+1} + H^+ + OH \quad (4)$$

producing Ag^{+1} and OH radical but the rate of its decomposition being slow the concentration of (Ag^{+1}) produced is small and because the concentration of $S_2O_8^{-2}$ is also reduced so is the amount of Ag^{+3} now formed by the reaction (1) above. Hence, the drop in the values of the rate constants is the latter part of the reaction is not possible. It is therefore concluded that the first product in these oxidations is Ag^{+3} an unstable intermediate which subsequently decomposes to give Ag^{+2} a stabler product.

In some of the oxidations strangely enough *viz.* ethanol and dioxane by peroxydisulphate catalysed by silver ion the reactions have been attended by an induction period. The following tables given such observations :

TABLE 5

(Ethyl alcohol) = 0·1 M $AgNO_3$ 0·001 M Dioxane 1 ml ($AgNO_3$) = 0·0005 M

($K_2S_2O_8$ = 0·02 M) values of the rate constant K/2·303 × 10^4	($K_2S_2O_8$ = 0·04 M) values of the rate constant K/2·303 × 10^4	$K_2S_2O_8$ = 0·01 M) value of the rate constant K/2·303 × 10^4	($K_2S_2O_8$ = 0·02 M) values of the rate constant K/2·303 × 10^4
16·20	8·80	18·10	12·40
13·45	36·85	39·73	45·25
33·03	57·97	48·48	61·93
49·15	64·53	54·18	71·65
56·50	66·31	54·99	73·72
65·50	56·13	55·46	73·07
65·30	63·58	54·99	70·69
64·27	61·77	63·46	85·87
61·26	59·86	-	67·37

The extent of the induction period is very much reduced when the experiments are carried out in the atmosphere of nitrogen showing that the dissolved oxygen inhibit the decomposition of Ag^{+3} thereby the necessary production of Ag^{+2} is delayed. In such reactions therefore it may be assumed that the catalytic activity is probably due to Ag^{+2} and not due to Ag^{+3}.

The results presented here, therefore, show that both bivalent and trivalent can be obtained by the interaction of potassium peroxydisulphate and silver nitrate solutions and one is led to believe that the catalytic action of silver ions for the reactions between this oxidant and a reducing substrate is mainly due to the formation of both bivalent and trivalent silver and their action depends upon the specific nature of the reducing substrate used in the investigation.

Acknowledgments

The author expresses his deep gratitude to Professor S. Ghosh, D.Sc., F.N.I., F.R.I.C. (London), F.N.A.Sc. for his kind and valuable suggestions and wishes to thank to the University Grant Commission, New Delhi for the award of a Senior Research Fellowship during the tenure of this work.

References

1. Yost *et al.* *J. Am. Chem. Soc.*, **59** : 2129, 1939.
2. Noyes *et al.* *J. Am. Chem. Soc.*, **59** : 1316, 1937.
3. T. Palagyi *et al.* *Acta Chimica Academicae Scientiarium Hungarical*, **30** (i) : 1-9, 1962.
4. Sutcliffe *et al.* *J. Phys. Chem.*, **56** : 1617, 1963.
5. Ray, P. and Sen, D. National Institute of Sciences of India Monograph "Chemistry of Bi and Tripositive silver", 1960.

Proc. Nat. Acad. Sci., India, 38(A), I & II, 1968.

Role of silver ions in the oxidation of organic compounds by peroxydisulphate

By

D. D. MISHRA

Department of Post-graduate Studies and Research in Chemistry, University of Jabalpur

Abstract

The silver catalysed oxidation of organic compounds *viz.* ethyl alcohol, lactic acid, glycerol and dioxane by peroxydisulphate involves the formation of trivalent silver as an intermediate and that its reaction with an organic substrate determines the rate of reaction. A plot for the values of energies of activation and entropies of activation suggests the existence of an isokinetic temperature. The reaction of these organic substrates towards their catalysed oxidation by peroxydisulphate are in the following decreasing order :

ethyl alcohol > lactic acid > glycol > dioxane > glycerol

The earlier publications[1] on the oxidations of these organic compounds contain the experimental procedure adopted for their kinetic investigations. Various authors[2] believe that the principal step, for the oxidation of a reducing substrate by peroxydisulphate catalysed by silver ion, is the interaction between monovalent silver ion and persulphate anion or monovalent silver ion and the radical SO_4^{-1}.

In the present investigation the rates of oxidation of ethyl alcohol, glycol, glycerol, lactic acid and dioxane have been found to be more or less proportional to the catalyst silver ion concentration and peroxydisulphate but the proportionate constants or velocity constants are certainly not the same and they have different energy of activation, temperature coefficients and entropy of activation. All these facts indicate that the rate determining step can not be the same reaction, for the oxidations of different organic compounds investigated here.

The first order rate constants for the oxidation of the monohydric alcohol ethyl alcohol, dihydric alcohol ethylene glycol and trihydric alcohol glycerol, with respect to peroxydisulphate for nearly the same concentrations of the above organic substrates, peroxydisulphate and the catalyst silver ion, are computed below :

TABLE 1

$K_2S_2O_8$ 0·02 M $AgNO_3$ 0·001 M Temperature 5°C

Orgrnic substance	Concentration of the reducing substrate	Values of the rate constants $K \times 10^4$ Min^{-1}
Glycerol	0·0570	26·05
Glycol	0·06	105·45
Ethyl alcohol	0·05	260.37

A perusal of the above table will clearly show that the oxidations proceed with different rates. As OH group in organic compounds has been known to be nuclophilic[3] it is expected that the oxidation should be rapid for polyhydric alcohols. Again, it has been found that for the oxidation of ethyl alcohol the order with respect to this compound is fractional but slightly positive but with either

glycol or glycerol the order with respect to these organic substrates is slightly negative indicating that higher concentration of these dihydric or trihydric alcohol possess an inhibitary effect on the reaction rate. In all the cases investigated the order of the reaction with respect to the organic compound can not be said to be zero order, though it tends to be so when the concentration of the organic compound is high as has been found for the oxidation of dioxane[4].

The values of rate controlling factors the energy of activation the entropy of activation and frequency factors for the oxidation of ethyl alcohol, glycol, glycerol lactic acid and dioxane are given in table 2.

TABLE 2

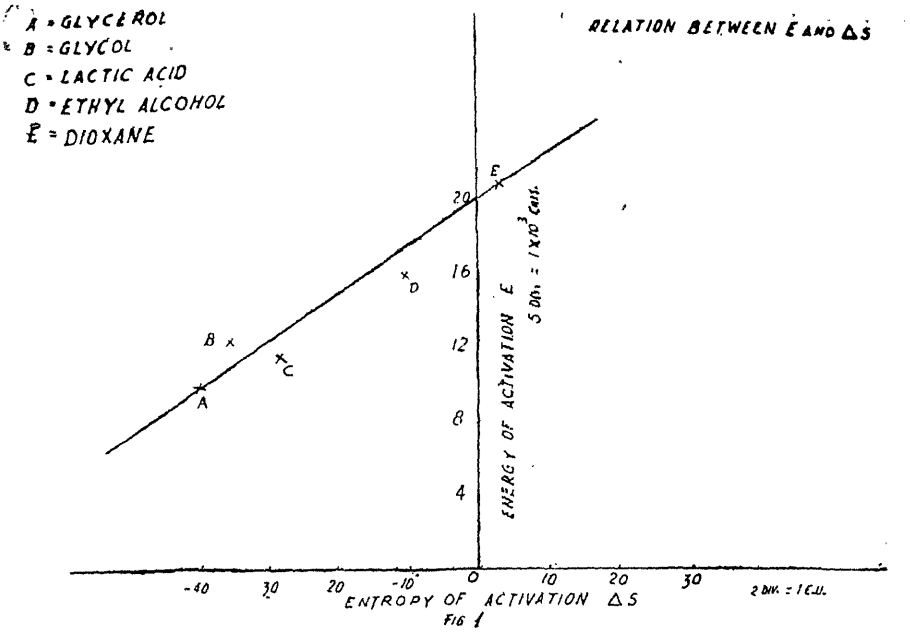
Reductant	Values of rate constant $K \times 10^4$ for unit concentration of silver nitrate (Temperature 35°C)	A $Mole^{-1}$ sec^{-1}	B $Mole^{-1}$ $cads^{-1}$	S E. U.
Glycerol	3·26	5803×10^2	8970	−39·96
Glycol	7·08	7582×10^3	12370	−35·93
Ethyl alcohol	43·64	1573×10^8	15920	−10·01
Lactic acid	9·41	1687×10^4	11280	−28·39
Dioxane	4·46	5593×10^{10}	20893	+3·4

It is evident from the above table that the rate of the oxidation of the various organic compounds are in the following decreasing order :

Ethyl alcohol > Lactic acid > Glycol > Dioxane > Glycerol

It is interesting to find that the values of the energy of activation for the polydric alcohols glycerol, glycol and the hydroxy acid lactic acid is comparatively low but the frequency factor is small yielding high negative values for the entropy of activation. On the other hand, for the organic substrates as Ethyl alcohol and Dioxane the energy of activation is comparatively large but the frequency factor is high with larger values for the entropy of activation for these reactions so much so that it is slightly positive for dioxane.

It has been found that glycerol, glycol and lactic acid possess high inhibitory effect on their own oxidation whilst this is not so for ethyl alcohol and dioxane. It is therefore clear that the action of Ag^{+3} or Ag^{+2} which is an intermediate product in the process of oxidation, acts differently for organic compounds investigated here. It may be concluded that an organic compound having a tendency to form a complex with Ag^{+3} will behave in the manner observed with glycerol, glycol and lactic acid. Oxalic acid is well known to form complex salts with silver and Ghosh *et al*[5] have reported the inhibitory effect of this organic substrate on its own oxidation by peroxydisulphate. Leffler[6] has recognised that in some cases there is a linear relationship between the variations of 'E' and ''$\triangle$S'. The values of 'E' and $\triangle$S obtained here have been plotted and represented in fig. 1. Considering the errors involved in finding the values of E and Δ S we may say that the plot is nearly a straight line, which may be represented by the relationship $E = T\triangle S +$ constant where T is the isokinetic temperature or the absolute temperature where the rates of all these reactions are the same. It may, therefore, be concluded that above the isokinetic temperature ethyl alcohol is more reactive than the polyhydric alcohols or lactic acid towards their oxidation processess. Infact the observations are likely to be reversed if the reactions are carried out below the isokinetic temperature *i.e.* −4°C. It may concluded that at 35°C the reactions of organic substrates towards their catalysed oxidation by peroxydisulphate are in the following decreasing order :



Ethyl alcohol > Lactic acid > Glycol > Dioxane > Glycerol

A mechanism for the action of silver ions as catalyst has been advanced (loc cit.) and it has been concluded that silver catalysed oxidation of peroxydisulphate involves the formation of trivalent silver as an intermediate and that its reaction with an organic substrate determines the rate of the reaction. As the free radicals from peroxydisulphate, water and even from the organic substrates are likely to be formed during the reaction, traces of impurities lead to the erratic nature of the oxidation and even dissolved oxygen appears to play a significant role in defining the rates and products of such oxidations. It is therefore, necessary to carry out these studies in aqueous solutions in an atmosphere of an inert gas like nitrogen.

Acknowledgements

The author expresses his deep gratitude to Prof. S. Ghosh, D.Sc. F.N.I., F.N.A.Sc., F.R.I.C. for his kind and valuable suggestions and also wishes to thank to the Council of Scientific and Industrial Research for the financial assistance.

References

1. Mishra and Ghosh. *Jour. Indian Chem. Soc.*, **41** : 397, 1964.
——— *Ibid* **41** : 402, 1964.
——— *The proceedings of the National Aeademy of Sciences India* **34** A (3) : 317–321, 1964.
2. Gupta and Ghosh. *J. Indian Chem. Soc.* **35** : 483, 1958.
Yost. *J. Am. Chem. Soc.* **48** : 152, 1926.
3. Robinson. *Salway Reports*, 439 1931.
4. Mishra and Ghosh. *Proceedings of the National Institute of Sciences, India* **51**-A (2) : 119, 1965.
5. Shrivastava and Ghosh. *Z. Physik. Chem.*, 202, 298, 1953.
6. Leffler. *J. Org. Chem.* **29** : 1202, 1955.